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Wet Oxidation and Ozonation of Specific Organic Pollutants

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demostrating new and improved methodologies that will meet these needs both efficiently and economically.

This bench-scale study was undertaken to assess the capability of wet oxidation and ozonation to reduce the concentrations of five typical organic priority pollutants which may be found in industral process wastewaters. The results of the experiments will aid the government and industry environmental control engineers in the selection of the appropriate technology for the treatment of several specific organic compounds which typify classes of priority pollutants in terms of molecular structure.

Additional information on the results of the study may be obtained by contacting:

David G. Stephan
Director
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Cincinnati

ABSTRACT

This study was undertaken to assess the utility of wet oxidation and ozonation in the treatment of wastewaters containing five typical priority pollutants. The pollutants, phenol; 2-chlorophenol; 4-nitrophenol; 1,2-dimethylphthalate and 1,2-dichloroethane were selected for study on the basis of their occurrence, structure, water solubility and volatility. The ability of the wet oxidation and ozonation processes to oxidize these pollutants in aqueous solution was studied using batch laboratory scale experiments.

The ozonation experiments were designed to investigate the influence of two initial pH levels of a single temperature (25°C) and ozone dosage rate. The results showed that 1,2-dichloroethane was rapidly volatilized and the remaining four pollutants could be removed to less than detectable concentrations, in 5 to 10 minutes, at initial ozone usage rates of 3.9 to 5.9 moles of ozone per mole of compound removed. However, in this study the removal rates were limited by the rate of ozone mass transfer, and a significant amount of total organic carbon remained in solution. This carbon was slowly oxidized and consisted primarily of formic, oxalic, muconic and maleic acids.

The wet oxidation results indicated that all five pollutants could be oxidized under the conditions of temperature (204°C to 260°C) and oxygen pressured studied. The removal rates depended on the substance and on temperature and were adequately described by semi-empirical, first order kinetics. Alkaline pH levels markedly increased the rate of specific pollutant removal. However, over a one hour reaction period, alkaline pH levels gave significantly lower removals for total organic carbon. Cupric ion (at 50 mg/ℓ) acted as a catalyst and increased the rate and extent of removal for specific pollutants and total organic carbon. A significant amount of organic carbon remained in solution after the specific pollutants had been removed. This carbon was slowly oxidized and consisted primarily of formic and acetic acids, acetaldehyde and acetone. Bioassay tests indicated that wet oxidation removed 90 to 99 percent of the substances responsible for acute toxicity to *Daphnia magna*.

Although acetic acid was a major end product of wet oxidation, it was not evident during ozonation. Conversely, oxalic acid was a relatively minor product during wet oxidation, but was very significant in ozonation.

A wet oxidation process was designed to treat a 37.8 ℓ/min (10 gal/min) of a high COD (70,000 mg/ℓ) petrochemical waste which was inhibitory to a biological treatment process. A detailed economic evaluation of this process indicated that an investor's interest rate of 20 percent could be attained at a treatment charge of \$69 per 1000 gallons (\$17.81 per cubic meter) or \$0.16 per pound of COD removed (\$0.35 per Kg COD removed).

CONTENTS

Disclaimer..
Foreword.. ii
Abstract..iii
Figures.. iv
Tables..vii
Acknowledgements.. x
....xii

1. Introduction..
   Objectives and Rationale.. 1
   Wet Oxidation.. 1
   Ozonation.. 4
   Reactions and Products.. 4
   7

2. Conclusions.. 10

3. Areas for Further Study.. 12

4. Experimental Approach..
   Experimental Scope.. 14
   Wet Oxidation: Materials and Methods.. 14
   Ozonation: Materials and Methods.. 17
   Analytical Methods.. 22
   24

5. Ozonation Results and Discussion.. 27
   Evaluation of Air Stripping During Ozonation.. 27
   Substance Removal Patterns During Ozonation.. 30
   Ozone Consumption.. 38
   Enhancement of Mass Transfer by Simultaneous Diffusion and Reaction of Ozone.. 40
   Organic Carbon Transformations During Ozonation.. 42

6. Wet Oxidation Results and Discussion.. 46
   Material Balances.. 46
   Wet Oxidation Substance Removal Patterns.. 52
   Organic Carbon Transformations During Wet Oxidation.. 79

7. Application of Wet Oxidation to Industrial Waste Treatment........ 90
   Process Description and Analysis.. 91
   Equipment Selection and Cost.. 93
   Economic Evaluation.. 98

CONTENTS (continued)

References..105
Nomenclature..110
Appendices
A. Material Balance Procedure and Numerical Example................118
B. Material Balance Results and Breakdown from Wet Oxidation Experiments....................................136

FIGURES

Number Page

1 Conceptual Relationship Between Process Costs and Influent Organic Concentration.............................. 2

2 Vapor Pressure of Water.. 5

3 Typical Wet Oxidation Reactors................................ 6

4 Schematic Diagram of the Experimental Wet Oxidation System..... 18

5 Reactor in Floor Stand... 19

6 Photograph of Disassembled Reactor............................ 20

7 Schematic Diagram of the Experimental Ozonation System......... 23

8 Phenol and TOC Destruction During Ozonation at pH 6............ 31

9 Phenol and TOC Destruction During Ozonation at pH 10........... 32

10 2-Chlorophenol and TOC Destruction During Ozonation at pH 6.. 33

11 2-Chlorophenol and TOC Destruction During Ozonation at pH 10... 34

12 4-Nitrophenol and TOC Destruction at pH 6 and 4-Nitrophenol Destruction at pH 10 During Ozonation...................... 35

13 Dimethylphthalate and TOC Destruction During Ozonation at pH 6.. 36

14 Organic Acid Profiles During Ozonation of Phenol at pH 10...... 43

15 Organic Acid Profiles During Ozonation of 2-Chlorophenol at pH 10... 44

16 Influence of Temperature on Phenol Destruction During Wet Oxidation...................................... 55

17 Influence of Temperature on 2-Chlorophenol Destruction During Wet Oxidation......................................56

FIGURES (continued)

Number Page

18 Influence of Temperature on 4-Nitrophenol Destruction During Wet Oxidation.......... 57

19 Influence of Temperature on Dimethylphthalate Destruction During Wet Oxidation.......... 58

20 Influence of Temperature on 1,2-Dichloroethane Destruction During Wet Oxidation.......... 59

21 Arrhenius Plots Based on Phasic Model, Initial Fast Reaction... 64

22 Influence of Temperature on TOC During Wet Oxidation of 2-Chlorophenol.......... 66

23 Influence of Temperature on COD Destruction During Wet Oxidation of 2-Chlorophenol.......... 67

24 Influence of Initial pH on 2-Chlorophenol Destruction During Wet Oxidation at 232°C.......... 69

25 Influence of Initial pH on TOC Destruction During Wet Oxidation of 2-Chlorophenol at 204°C.......... 70

26 Influence of Initial pH on COD Destruction During Wet Oxidation of 2-Chlorophenol at 232°C.......... 71

27 Influence of Initial pH on Chloride Generation During Wet Oxidation of 2-Chlorophenol at 232°C.......... 72

28 Influence of Copper Catalyst on 2-Chlorophenol Destruction During Wet Oxidation at 204°C.......... 73

29 Influence of Copper Catalyst on TOC Destruction During Wet Oxidation of 2-Chlorophenol at 204°C.......... 74

30 Influence of Copper Catalyst on Dimethylphthalate Destruction During Wet Oxidation at 204°C.......... 75

31 Influence of Copper Catalyst on COD Destruction During Wet Oxidation of Dimethylphthalate at 260°C.......... 76

32 Organic Carbon Transformations During Wet Oxidation of 1,2-Dimethylphthalate at 204°C.......... 77

FIGURES (continued)

Number Page

33 Organic Carbon Transformations During Wet Oxidation of 1,2-Dimethylphthalate at 204°C with 50 mg/ℓ Copper Catalyst.. 78

34 Organic Carbon Transformations During Wet Oxidation of Phenol at 232°C.. 81

35 Organic Carbon Transformations During Wet Oxidation of 2-Chlorophenol at 232°C.................................. 82

36 Comparison of Chromatograms of Petrochemical Waste Extracts Before and After Wet Oxidation............................ 85

37 Process Flow Diagram Showing Mass Rates (Basis 1 Minute)...... 92

38 Variation of Reactor Pressure with Liquid Feed Inlet Temperature.. 94

39 Variation of Mass Rate of Water in Reactor Vapor Product Stream with Reactor Feed Inlet Temperature......... 95

40 Feed Preheat Exchanger Cost in Thousands of Dollars versus Reactor Feed Temperature........................... 96

41 Process Flow Diagram Showing Temperatures and Pressures........ 97

42 Variation of IIR with Treatment Charges......................102

43 Sensitivity of Investor's Interest Rate with Respect to Changes in Capital Investment, Operating Expenses and Income...103

TABLES

Number | | Page
1 Scope of Wet Oxidation Experiments.......... 15

2 Alkaline pH Adjustment of Wet Oxidation Experiments.......... 16

3 Scope of Ozonation Experiments.......... 16

4 Typical Peak Retention Times for Butyl Esters.......... 25

5 Measured and Predicted Relative Concentrations During Air Stripping.......... 28

6 Values of Henry's Constant Used to Calculate Predicted Relative Concentrations.......... 29

7 Parameter Estimates for Specific Substance and Total Organic Carbon Removal Parameters.......... 37

8 Initial Rates of Ozone and Reactant Utilization.......... 39

9 Calculated Values of the Enhancement Factor Assuming That Ozone is Used Only by Reaction with Phenol and Phenolate.... 42

10 2-Chlorophenol Material Balance Results.......... 48

11 Summary of Material Balance Results.......... 49

12 2-Chlorophenol Material Balance Breakdown.......... 50

13 First Order Model Removal Parameters, m_1, and Standard Error Values, s, for Wet Oxidation of Specific Substances... 60

14 Phasic Model Removal Parameters, m_f, for Initial Fast Reaction for Wet Oxidation of Specific Substances.......... 60

15 Summary of Activation Energy Values Based on Phasic Model, Initial Fast First Order Reaction.......... 65

TABLES (continued)

Number Page

16 Literature Values of Activation Energies for Wet Oxidation 65

17 Modified First Order Removal Parameters, m_2 and C^*, for TOC Removal Patterns During Wet Oxidation 63

18 Influence of Initial pH on Wet Oxidation Removal Parameter Estimates, m_1, m_2 and C^* 68

19 Influence of Copper Catalyst on Kinetic Removal Parameters 80

20 Characteristics of Petrochemical Waste Before and After Wet Oxidation 84

21 Comparison of Organic Constituents in Petrochemical Wastewater Extract Before and After Wet Oxidation 87

22 Results of *Daphnia* Bioassays on Solutions of Specific Substances After Wet Oxidation 89

23 Equipment Cost Summary 98

24 Total Capital Investment Summary 99

25 Annual Income and Operating Expense Summary 100

26 Influence of Wet Oxidation Treatment Charges on IIR 104

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Nina Albanese contributed to the material balance calculations.

Deborah McDowell drafted most of the figures; Jeanine Godfried and Mary Ann Johnson typed the report manuscript.

SECTION 1

INTRODUCTION

OBJECTIVES AND RATIONALE

Section 307 of the 1977 Amendments to the Federal Water Pollution Control Act (PL 95-217) focused attention on the removal and fate of specific organic and inorganic pollutants (i.e. priority pollutants) contained in wastewater discharges. This report presents the results of a study undertaken to assess the applicability of wet oxidation and ozonation to the treatment of wastewater containing specific pollutants typical of the 114 organic compounds included on the EPA priority pollutant list (1).

Possible processes for the removal of organic pollutants include carbon adsorption, air stripping and destruction by oxidation (2,3). Oxidation has an inherent advantage over adsorption and stripping in that removal and destruction are carried out simultaneously. Several oxidation processes have potential application for the destruction of organic pollutants. These are:

Chemical oxidation using agents such as ozone

Biological oxidation

Wet oxidation at high temperatures and pressures

Incineration

The choice of which process is best suited to a waste stream will depend upon the nature of the particular waste and the concentration of the stream. Figure 1 shows a conceptual relationship between process cost and concentration of organic pollutant (4). For low concentrations of labile organics, chemical oxidation may be suitable. For higher concentrations of biodegradable organic compounds, biological oxidation processes such as activated sludge may be most cost effective. As the concentration of organic material increases beyond 30%, high temperature incineration becomes practical. Wet oxidation is ideally suited to liquid wastes which are too dilute to incinerate by dry combustion and too concentrated or refractory to handle by chemical and biological oxidation.

Although most of the organic priority pollutants are biodegradable (5), suitable acclimation of a bacterial culture or biological treatment process may be necessary. Because of this, biological treatment may be ineffective in removing these substances when their sporadic presence prevents proper acclimation. The non-biological processes will, therefore, tend to be more applicable to aqueous waste treatment in situations where:

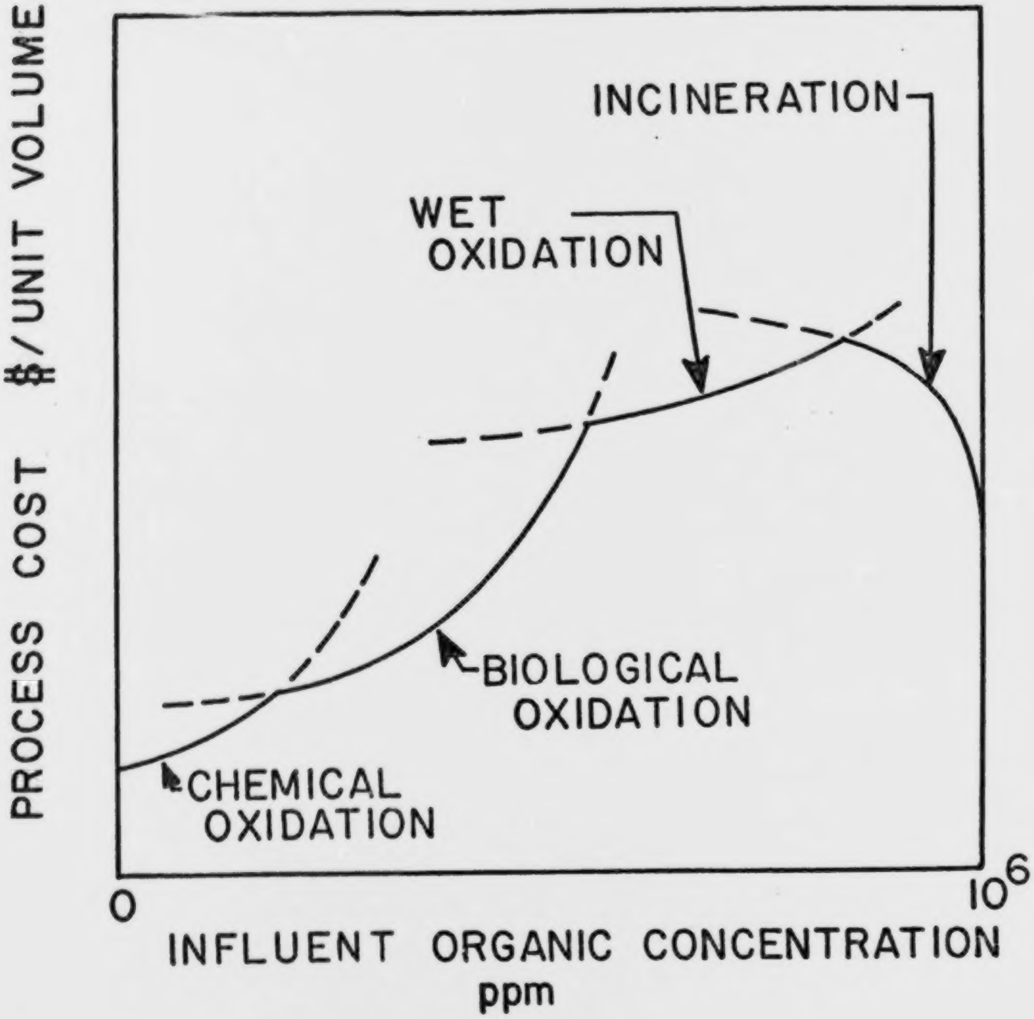


Figure 1. Conceptual Relationship Between Process Costs and Influent Organic Concentration.

Specific pollutants are not biodegradable.

Waste streams containing high concentrations of certain organic priority pollutants are produced sporadically.

Specific pollutants are present at concentration levels which inhibit biological treatment.

Total concentration of organics is high enough to favor the economics of wet oxidation or incineration.

The objective of this research was to assess the utility of the wet oxidation and ozonation processes in the treatment of wastewaters containing typical priority pollutants. In the case of wet oxidation, efforts were made to determine the influence of temperature, pH value, catalyst, and reaction time on the degree of pollutant destruction. For ozonation, information was developed on the degree of pollutant destruction as influenced by ozone dosage and contact time. For both processes, the fate of the pollutants were studied by measuring products of incomplete oxidation.

Five compounds were selected as typical priority pollutants for this study. Various criteria were employed in selecting the specific compounds to be studied. Ideally, the substances should be significant pollutants in themselves and typify a class of priority pollutants in terms of molecular structure. In addition, since the oxidation processes being studied involve gas-liquid transfer and liquid phase reaction, it was desired that the substances be at least moderately soluble in water and exhibit low volatility. The compounds and the rationale for their selection were:

Substance	Rationale
Phenol	Important pollutant; subject of several previous wet oxidation and ozonation studies, provided a good basis for comparison Extremely soluble in water (80,000 mg/ℓ) Low volatility
2-Chlorophenol	Typical chlorinated phenol Very soluble in water (28,000 mg/ℓ) Moderate volatility
4-Nitrophenol	Typical nitrated phenol Very soluble in water Low volatility
1,2-Dimethylphthalate	Typical phthalate Moderately soluble in water (5000 mg/ℓ) Low volatility

1,2-Dichloroethane	Typical chlorinated hydrocarbon Moderately soluble in water (8700 mg/ℓ) High volatility

In general, the substances met the selection criteria; 1,2-dichloroethane was an exception because of its high volatility. However, this property proved to be useful because it illustrated the difference between the behavior of volatile and non-volatile substances during wet oxidation and ozonation.

WET OXIDATION

The wet oxidation process relies on conditions of elevated temperature and pressure to oxidize organic substances in aqueous solution. Temperature is recognized as the most important process parameter (6). Pressure is required to maintain water in the liquid state and to provide a minimum overpressure of oxygen. Figure 2 shows the well-known relationship between water vapor, pressure and temperature. At any given temperature, the reactor pressure must exceed the stream pressure by an amount sufficient to provide a satisfactory oxygen overpressure. The oxygen pressure required will depend on the rate of the wet oxidation reaction and on the mass transfer characteristics of the reactor. The total pressure required is determined by the reactor material and energy balances. Typical conditions for wet oxidation range from 200°C and 4 MPa to 315°C and 15 MPa. The higher temperatures and pressures enhance the rates of both oxygen transfer (6) and reaction at the expense of greater equipment and compressor power costs. The corrosion resistance of reactor and heat exchanger materials under conditions of high temperature and oxygen pressure has been a fundamental problem in the application of wet oxidation to wastewater treatment. Because of this, relatively high cost corrosion resistant materials such as titanium are frequently employed.

Wet oxidation is not a new process. Its origins can be traced to the Strehlenert Process of wood technology (7) patented in 1915 and to the zinc sulfide oxidation process of hydrometallurgy patented in 1927 (8). Figure 3 shows two typical wet oxidation reactors, the bubble tower and the stirred tank cascade system. The tower system has been applied to several full scale installations (6) and the cascade system has been employed on a more limited basis to treat sludges (9), munitions waste (10) and industrial wastewater (11).

OZONATION

Wet oxidation and ozonation are similar in that both processes accomplish oxidation of organic matter in aqueous solution. Whereas the wet oxidation process employs an excursion in temperature and pressure to establish favorable conditions for dissolved oxygen to react, ozonation relies on the oxidation potential of dissolved ozone at ambient temperatures and pressures. Typically, ozonation involves contacting the wastewater with an air or oxygen stream

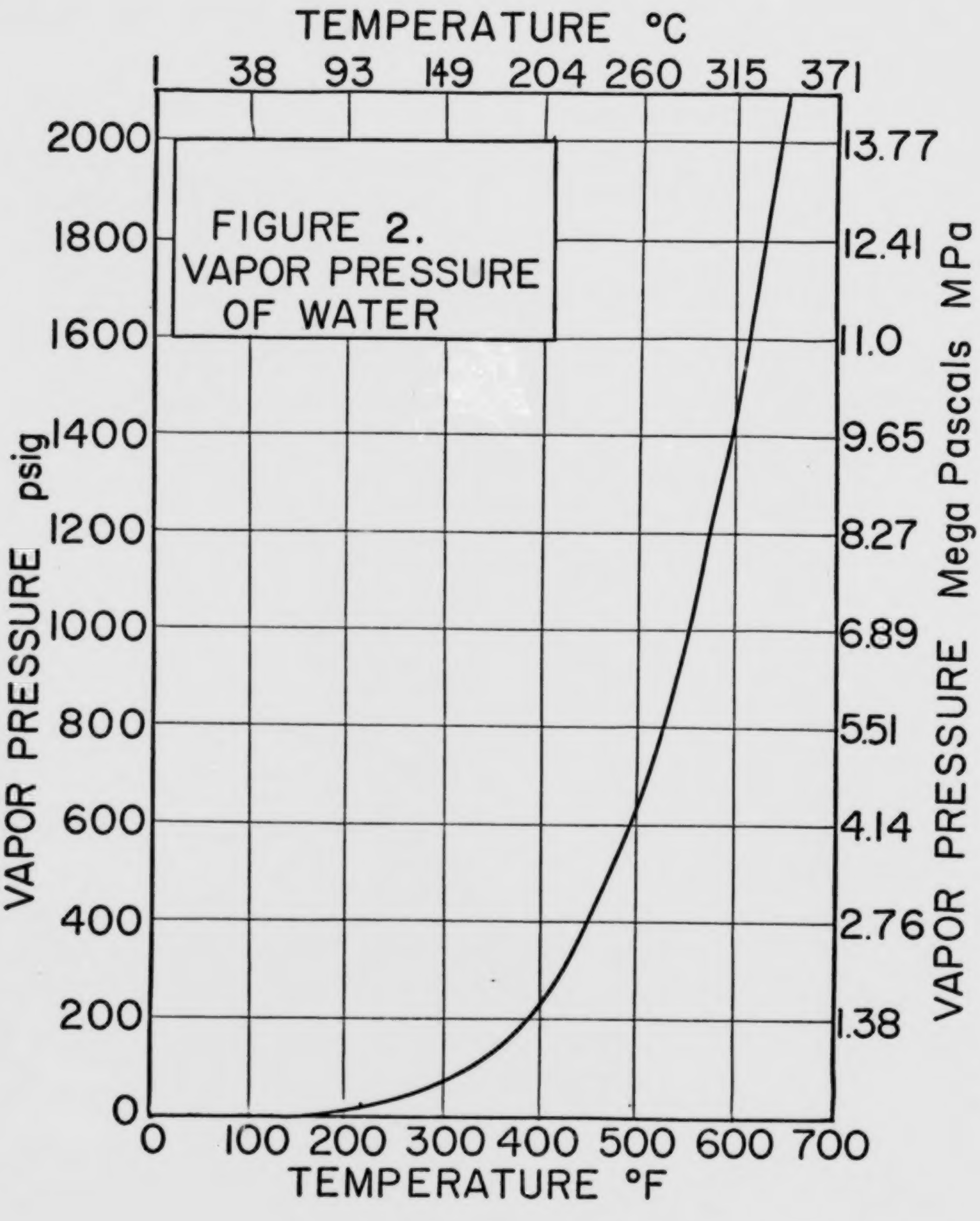
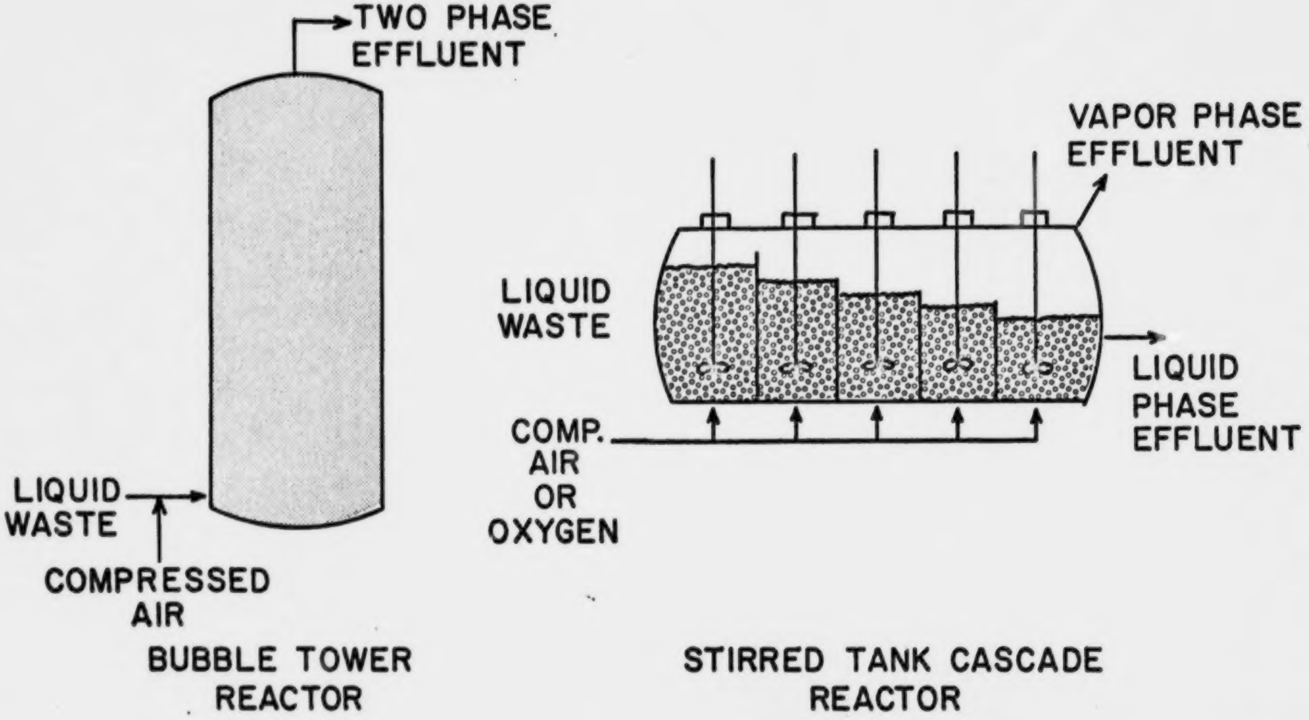


Figure 2. Vapor Pressure of Water.


TWO PHASE EFFLUENT
LIQUID WASTE
COMPRESSED AIR
VAPOR PHASE EFFLUENT
LIQUID WASTE
COMP. AIR OR OXYGEN
LIQUID PHASE EFFLUENT

BUBBLE TOWER REACTOR

STIRRED TANK CASCADE REACTOR

Figure 3. Typical Wet Oxidation Reactors.

containing 2 to 5% ozone. Both processes have application in the removal of specific organic substances from aqueous waste streams. Ozonation would be expected to offer economic advantages over wet oxidation for more dilute wastes. As the concentration of oxidizable organic matter increases to roughly 3%, the wet oxidation process becomes thermally autogenous and further increases in concentration of oxidizable organic matter can lead to energy recovery.

Additional similarities between the processes are that each involves interphase mass transfer of oxidant from the gas to the liquid state and the rate of each may be limited by the rate of mass transfer. Furthermore, each process has been reported to produce a residual of low molecular weight organic acids which are oxidized only slowly. Finally, it has been hypothesized by various investigators that free hydroxyl radicals play an important role in the reactions of each process.

REACTIONS AND PRODUCTS

Rice and Browning (12, 13) have compiled an extensive literature review of the reactions occurring and products produced during ozonation of various classes of organic compounds. It has been reported that ozone reacts with aromatic compounds to produce catechol and hydroquinone followed in turn by muconic, maleic, glyoxylic, glycolic, oxalic and formic acids. The corresponding aldehydes have frequently been detected as precursors of these acids. Because the lower molecular weight acids generally react more slowly than their parent compounds, the rate of total organic carbon removal decreases with time. Although it has been reported that formic acid is readily converted to CO_2 by ozone, Japanese workers (14) have recently observed formic acid to be the major organic product produced during ozonation of phenol.

Considerable research has been done on wet oxidation of common waste materials and sewage sludges. However, many of the literature reports relate to proprietary wet oxidation processes and are difficult to interpret. Teletzke et al. (15) studied the wet air oxidation products of sewage sludge and determined that the complex polymeric organic fraction of sludge was initially degraded to simple constituent compounds which were subsequently degraded. At temperatures below 190°C, starch was degraded most extensively whereas lipids were the most resistant and protein and crude fiber were intermediate. Hydrolysis as well as oxidation played an important role in the destruction of the complex polymeric organic compounds initially present. Nearly all known amino acids were found free or as polypeptides in raw sludge. At intermediate degrees of oxidation, most known amino acids were formed while under more severe conditions, only glycine, beta-alanine and gamma-aminobutyric remained.

Fassell (9) also reported on the wet oxidation products produced from sludge. He found that the residual organics remaining in the liquid effluent consisted primarily of acetic acid with lesser amounts of propionic acid, formic acid and acetone. The vapor phase condensate also contained acetic and propionic acid with trace amounts of butyric acid, acetaldehyde, acetone, formic acid, methanol and ethanol. Fassell indicated that the cascade reactor system which he studied had the potential to greatly reduce the cost of sludge processing through the possible recovery of ammonia, acetate and metals.

Others have studied the wet oxidation of phenol (16), glucose (17,18,19), shipboard wastes (20), brewery wastes (21) and propionic acid (22). More recently, Randall and Knopp (23) used Daphnia bioassays to study detoxification of specific organic substances by wet oxidation and found the process to be very effective.

Various investigators have hypothesized free hydroxyl radicals to play an important role in the reactions of wet oxidation (24,17) and ozonation (25). In view of this, one might expect similarities between the reaction products produced by each process.

Ozonation Kinetics

The kinetics of ozonation reaction have been expressed as (25,26):

$$r = (k_o)(C)(O_3) \qquad 1$$

where: r = rate of reaction per unit volume, mol L^{-3} t^{-1}

k_o = reaction rate constant, L^3 mol^{-1} t^{-1}

C = aqueous concentration of specific substance at time t, mol L^{-3}

O_3 = aqueous concentration of ozone, mol L^{-3}

L = length dimension

t = time dimension

mol = g. mole

g = gram

For phenol, the reaction rate constant has been shown to increase with pH. A reasonable explanation is that as pH increases above 3, ozone decomposes to form highly reactive hydroxyl radicals and phenol ionizes to form the more reactive phenolate ion (pK = 9.9). Hoigne' and Bader (25) have proposed a reaction scheme in which ozone itself reacts directly and selectively with specific organics at low pH values. At higher pH values, the reaction is less selective and is accomplished by the decomposition products of ozone such as hydroxyl radicals. The following values have been given for ozonation rate constants (26):

Phenol: 400 ℓ/mol·sec (20°C, low pH, direct reaction)

2-Chlorophenol: 200 ℓ/mol·sec (20°C, low pH, direct reaction)

Phenolate ion: 1.3×10^7 ℓ/mol·sec

Gurol (26) recently studied the kinetics of ozone decomposition and reaction with phenol and developed a mathematical model to predict the profiles of phenol, muconic acid, hydroquinone and catechol during semi-batch ozonation experiments at pH 3. At higher pH values, the model failed to describe the observed profiles, presumably because the reaction rates were increased to the point where a significant amount of ozone reacted in the film and enhanced the mass transfer rate.

Others (27,28) have described the phenol profile during semi-batch ozonation by:

$$\frac{dC}{dt} = (K_c)(F)C \qquad 2$$

where: K_c = combined rate constant, mol phenol (mol ozone)$^{-1}$

F = dosage rate, mol ozone min^{-1} (mol phenol initially present)$^{-1}$

This expression combines the effects of mass transfer and reaction and, because of this, the combined rate constant, K_c, is system specific.

Wet Oxidation Kinetics

Many of the literature reports on wet oxidation do not lend themselves to kinetic interpretation because they are concerned with heterogeneous mixtures such as sludge or are based on nonspecific measures such as chemical oxygen demand. However, a few studies on pure substances have been reported.

Pruden and Le (16) expressed the kinetic rate equation for wet oxidation of phenol as:

$$r = k_w(C)(O_2) \qquad 3$$

where: k_w = wet oxidation reaction rate constant, L^3 mol^{-1} t^{-1}

O_2 = aqueous concentration of oxygen, mol L^{-3}

These workers evaluated oxygen in terms of the volumetric mass transfer coefficient (29), K_La, and Henry's constant to develop a flow reaction model which was supported by their data. Ploos van Amstel (18) studied wet oxidation of glucose and, based on an apparent half-order dependence of the reaction rate on glucose concentration. concluded that the reaction took place in the diffusive film and was mass transfer limited. Recently, Skaates _et al_. (19) pointed out that this half-order dependence is in accordance with a reaction following the kinetics of Equation 3, taking place within the diffusive film.

Sadana and Katzer (56) studied the wet oxidation of phenol in the presence of solid copper oxide catalyst over the temperature range of 96°C to 146°C and reported that, during the rapid oxidation phase, the reaction rate was first order with respect to phenol and half order with respect to oxygen pressure.

SECTION 2

CONCLUSIONS

Semi-batch ozonation experiments showed that:

1. All four specific pollutants studied could be removed to less than detectable concentrations (in 5 to 10 minutes) through ozonation. However, the removal rates were limited by the rate of ozone mass transfer.

2. During the initial stages of the ozonation experiments, reaction in the diffusive film enhanced the mass transfer rate.

3. A significant amount of total organic carbon remained in solution after the specific pollutants had been removed and this carbon was slowly oxidized. Formic, oxalic, muconic and maleic acids accounted for roughly one-quarter to three-quarters of the organic carbon remaining.

4. Initial ozone utilization ratios showed that 3.9 to 5.9 moles of ozone per mole of specific pollutant were consumed.

5.. Increasing the initial pH from 6 to 10: a) increased the specific pollutant removal rate for phenol and 4-nitrophenol, but decreased the rate for 2-chlorophenol and b) decreased the total organic carbon removal rates for phenol and 2-chlorophenol.

Batch wet oxidation experiments showed that:

1. All five specific pollutants studied could be oxidized under the conditions of temperature and oxygen pressured studied. The removal rates depended on the substances and on temperature and were adequately described by semi-empirical first order kinetics. At 232^{o}C, the first order removal parameter varied from a low of 0.09 min^{-1} for 1,2-dimethylphthalate to a high of 0.84 min^{-1} for 1,2-dichloroethane. The removal rates increased with temperature according to the Arrhenius relationship. Values of the activation energy ranged from a low of 7.9 Kcal/mol for phenol to a high of 28.8 Kcal/mol for 4-nitrophenol.

2. Alkaline pH levels markedly increased the rate of specific pollutant removal and only slightly increased the rate of total organic carbon removal. However, over the one hour reaction period, alkaline pH levels gave markedly lower removals for total organic carbon and chemical oxygen demand.

3. Cupric ion acted as a catalyst and increased the rate and extent of removal of specific pollutants and total organic carbon.

4. Reaction in the diffusive film probably did not enhance the mass transfer of oxygen in the stirred-unsparged pressure reactor.

5. A significant amount of total organic carbon remained in solution after the specific pollutants had been removed and this carbon was slowly oxidized. More than three-fourths of this carbon was accounted for by low molecular weight acids, acetaldehyde and acetone.

6. Bioassay tests using *Daphnia magna* indicated that wet oxidation achieved 90 to 99 percent detoxification for phenol, 2-chlorophenol and 4-nitrophenol.

Although acetic acid was a major end product of wet oxidation, it was not evident during ozonation. Conversely, oxalic acid was a relatively minor product during wet oxidation, but was very significant in ozonation.

A wet oxidation process was designed to treat a 37.8 ℓ/min (10 gal/min) at a high COD (70,000 mg/ℓ) petrochemical waste which was inhibitory to a biological treatment process. A detailed economic evaluation of this process indicated that an investor's interest rate of 20% could be attained at a treatment charge of \$69 per 1000 gallons (\$17.81 per cubic meter) or \$0.16 per pound of COD removed (\$0.35 per Kg COD removed).

SECTION 3

AREAS FOR FURTHER STUDY

The information presented in this report indicates that both wet oxidation and ozonation could be useful in the treatment of certain aqueous wastes containing typical organic priority pollutants. However, there are certain areas of uncertainty in which additional study is warranted.

For wet oxidation, the following questions should be addressed:

1. What are the reaction mechanisms involved and why is a substantial fraction of the organic carbon converted to organic acids instead of carbon dioxide? A better understanding of the mechanism might lead to process modifications which would promote more complete oxidation.

2. What are the values of solubility in water and Henry's constant for various specific pollutants and reaction products at high temperatures? This information is necessary to predict the degree of volatilization or air stripping which would occur in a continuous wet oxidation process. Likewise, better information on the oxygen transfer coefficient at high temperature would be helpful in reactor design.

3. For a given aqueous waste stream and wet oxidation process configuration, what is the optimal process design to achieve a given degree of pollutant removal and/or COD removal? This would require that a process model, similar to the one developed in Section 7 of this report, be optimized to minimize the treatment cost.

4. How might powdered activated carbon be used to adsorb pollutants from a dilute wastewater and be concentrated prior to regeneration by wet oxidation? This concept is attractive because it could make wet oxidation feasible for more dilute wastewater streams. The key question to be answered here is how the powdered carbon could be concentrated before regeneration by wet oxidation.

5. What is the effectiveness of operating full scale wet oxidation systems employed for removal of toxic pollutants? A few such systems are or will soon be in operation. Their effectiveness should be studied and documented.

The ozonation process has received more study than has wet oxidation and, therefore, more is known about the reaction mechanisms involved in ozonation. In addition, the engineering analysis of an ozonation system is fundamentally simpler than that of a wet oxidation system. Although additional information on ozone reaction mechanisms would be useful, it appears that the main area for further study should concentrate on ways to improve mass transfer of ozone from the gas to the liquid phase.

SECTION 4

EXPERIMENTAL APPROACH

EXPERIMENTAL SCOPE

The experimental phase of this study consisted of several batch wet oxidations and semi-batch ozonations of aqueous solutions of five specific organic substances; phenol, 2-chlorophenol, 4-nitrophenol, 1,2-dimethylphthalate and 1,2-dichloroethane. All five were subjected to wet oxidation; however, 1,2-dichloroethane was readily removed by air stripping and therefore was not ozonated.

Wet Oxidation

The wet oxidation experiments were designed to investigate the influence of temperature, initial pH and presence of copper catalyst on the wet oxidation process. Forty-four batch wet oxidation experiments were conducted under the experimental conditions indicated in Table 1 where each "X" represents a batch wet oxidation experiment.

Temperature: Three temperatures were selected; 204°C, 232°C and 260°C. For three of the substances, replicate control runs were conducted at each temperature. The data from these replicate control runs were averaged to provide a basis for comparison with the other treatments.

Initial pH: Two initial pH levels were selected, control (pH 4.5) and alkaline. The control pH of 4.5 was achieved by addition of the reactant to distilled water. The alkaline pH was obtained by addition of sodium hydroxide. The quantity of sodium hydroxide added and the resulting initial pH varied between substances shown in Table 2.

Catalyst: Cupric ion was chosen to study the influence of catalyst on the wet oxidation process. The catalyst concentration was usually 50 mg/ℓ of copper (added as $CuSO_4 \cdot 5H_2O$).

Ozonation

The ozonation experiments were designed to investigate the influence of two initial pH levels (6 and 10) at one temperature (25°C) and ozone dosage rate. Seventeen ozonation experiments were conducted under the conditions indicated in Table 3. Additional experiments were performed to study air stripping. Initial pH values of 6 and 10 were obtained by dissolving the or-

TABLE 1. SCOPE OF WET OXIDATION EXPERIMENTS

Substance	Temperature °C	Experimental Conditions Control	Alkaline	Copper Catalyst
Phenol	204	2X		X^{100}
	232	3X	X	X^{100}
	260	2X		X^{100}
2-Chlorophenol	204	2X	X	X
	232	2X	X	X
	260	2X		
4-Nitrophenol	204	X, X*		X
	232	2X, 2X*		X
	260	2X		
1,2-Dimethylphthalate	204	X		X, X^{500}
	232	X*	X*	
	260	X*		X^{100}, X^{500}
1,2-Dichloroethane	204	X		
	232	X	X	X
	260	X		

* Initial concentration was 1000 mg/ℓ, all others were at an initial concentration of 5000 mg/ℓ.

100 Catalyst concentration was 100 mg/ℓ copper

500 Catalyst concentration was 500 mg/ℓ copper; all others were at a catalyst concentration of 50 mg/ℓ copper.

TABLE 2. ALKALINE pH ADJUSTMENT OF WET OXIDATION EXPERIMENTS

Substance	NaOH Added for Alkaline Treatment (g/ℓ)	Initial Alkaline pH
Phenol	10.0	13.0
2-Chlorophenol	3.2	9.5
4-Nitrophenol	-	-
1,2-Dimethylphthalate	2.0	12.0
1,2-Dichloroethane	10.0	13.0

TABLE 3. SCOPE OF OZONATION EXPERIMENTS

Substance	Initial pH	
	6	10
Phenol	2X	2X
2-Chlorophenol	4X	2X, X*
4-Nitrophenol	3X	X
1,2-Dimethylphthalate	X	X

* Initial concentration was 1000 mg/ℓ, all others were at an initial concentration of 50 mg/ℓ. All at 25°C.

ganic reactant in the following phosphate buffer solutions:

pH 6: 0.10 M KH_2PO_4, 1.1×10^{-2} M NaOH

pH 10: 0.05 M Na_2HPO_4, 1.5×10^{-3} M NaOH

The ionic strength of each solution was approximately 0.15.

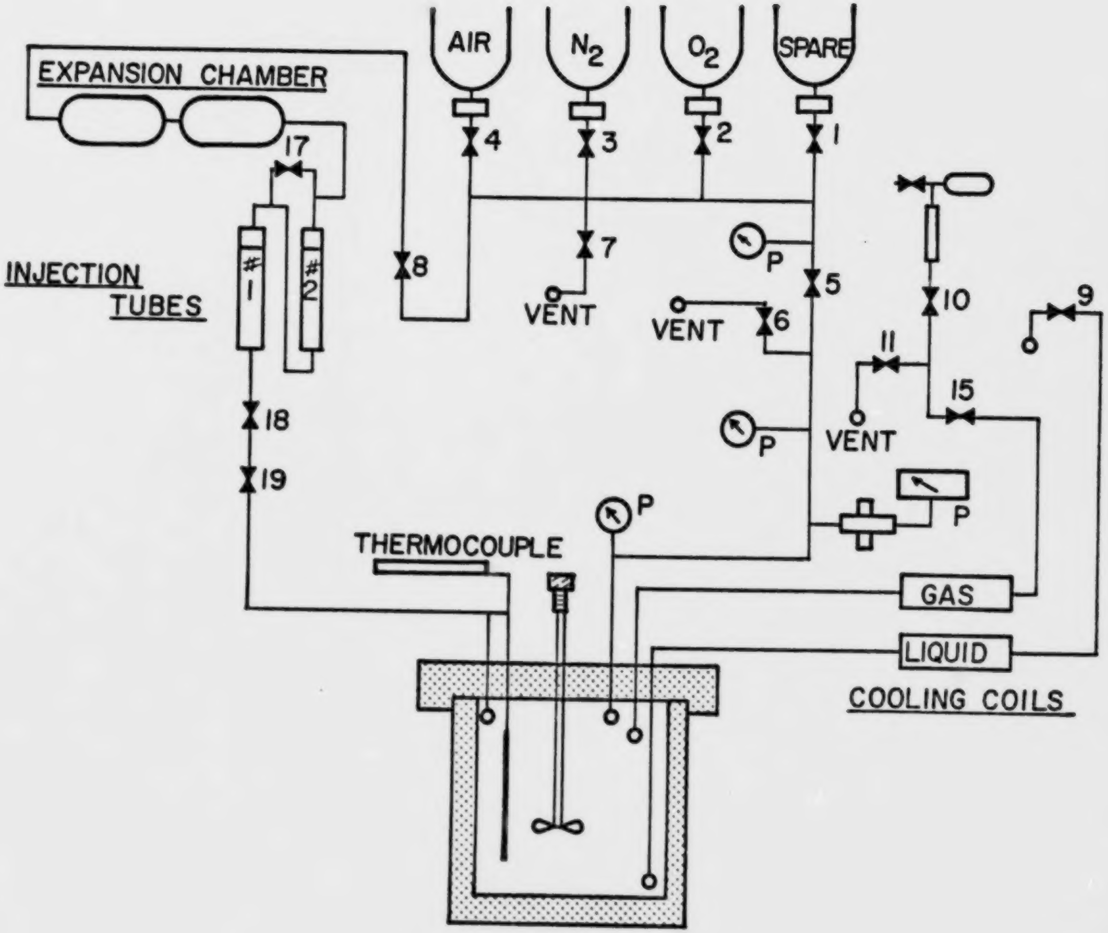
Measured Responses

In both the wet oxidation and ozonation experiments, the primary measured responses were the time profiles of specific reactant, certain intermediate products and total organic carbon (TOC). Chemical oxygen demand (COD) was also measured during the wet oxidation experiments. For purposes of comparison, these time profiles were fit by empirical first order models. An initial rate approach was employed to interpret the results in terms of the reaction kinetics.

At the conclusion of the wet oxidation experiments, the gas phase was analyzed and, because the wet oxidation reactor was a closed batch system, it was possible to strike material balances for carbon, oxygen and chlorine. During the ozonation experiments, the exit gas was passed through potassium iodide traps and the cumulative amount of ozone in the exit gas was measured. In several runs, the traps were changed at two minute intervals so that the ozone consumption rate could be determined as a function of time.

WET OXIDATION: MATERIALS AND METHODS

The wet oxidation reactor was a stirred 1.8 liter titanium vessel (Parr Instrument Company) equipped with automatic temperature control, variable speed stirrer and tachometer. Stirring speed was set at 500 rpm for all runs. Figure 4 shows a diagram of the reactor along with the sampling and injection system. Figures 5 and 6 are photographs of the reactor in the floor stand and disassembled reactor, respectively. The reactor was charged with 900 ml of distilled water, purged with oxygen, sealed and brought to a stable condition at the desired temperature. A 50 ml solution of reactant was loaded into injection tube 1 and a 50 ml distilled water wash was placed into injection tube 2. Injection was accomplished by pressurizing the injection system with oxygen and using this pressure to sequentially force the contents of both tubes into the reactor. The initial concentration of organic reactant was normally 5000 mg/ℓ and the initial oxygen pressure was set so that the 0.8 liter headspace contained enough oxygen to completely oxidize the reactant and still maintain at least a 0.34 MPa (50 psia) oxygen overpressure. The initial and final total pressures, therefore, depended on the reactant and temperature. Typical values of initial pressure were 3.9 MPa (580 psig) at 204°C, 5.2 MPa (760 psig) at 232°C and 7.1 MPa (1050 psig) at 260°C. Liquid samples were


AIR
N2
O2
SPARE
EXPANSION CHAMBER
INJECTION TUBES
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1
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18
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P
THERMOCOUPLE
GAS
LIQUID
COOLING COILS

Figure 4. Schematic Diagram of the Experimental Wet Oxidation System.

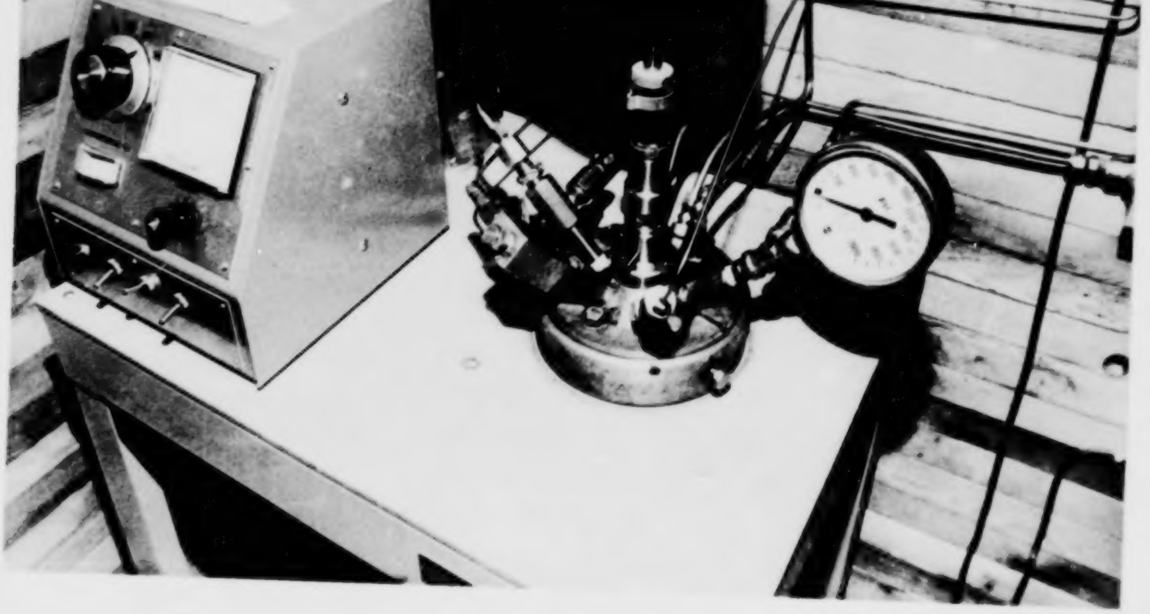


Figure 5. Reactor in Floor Stand.

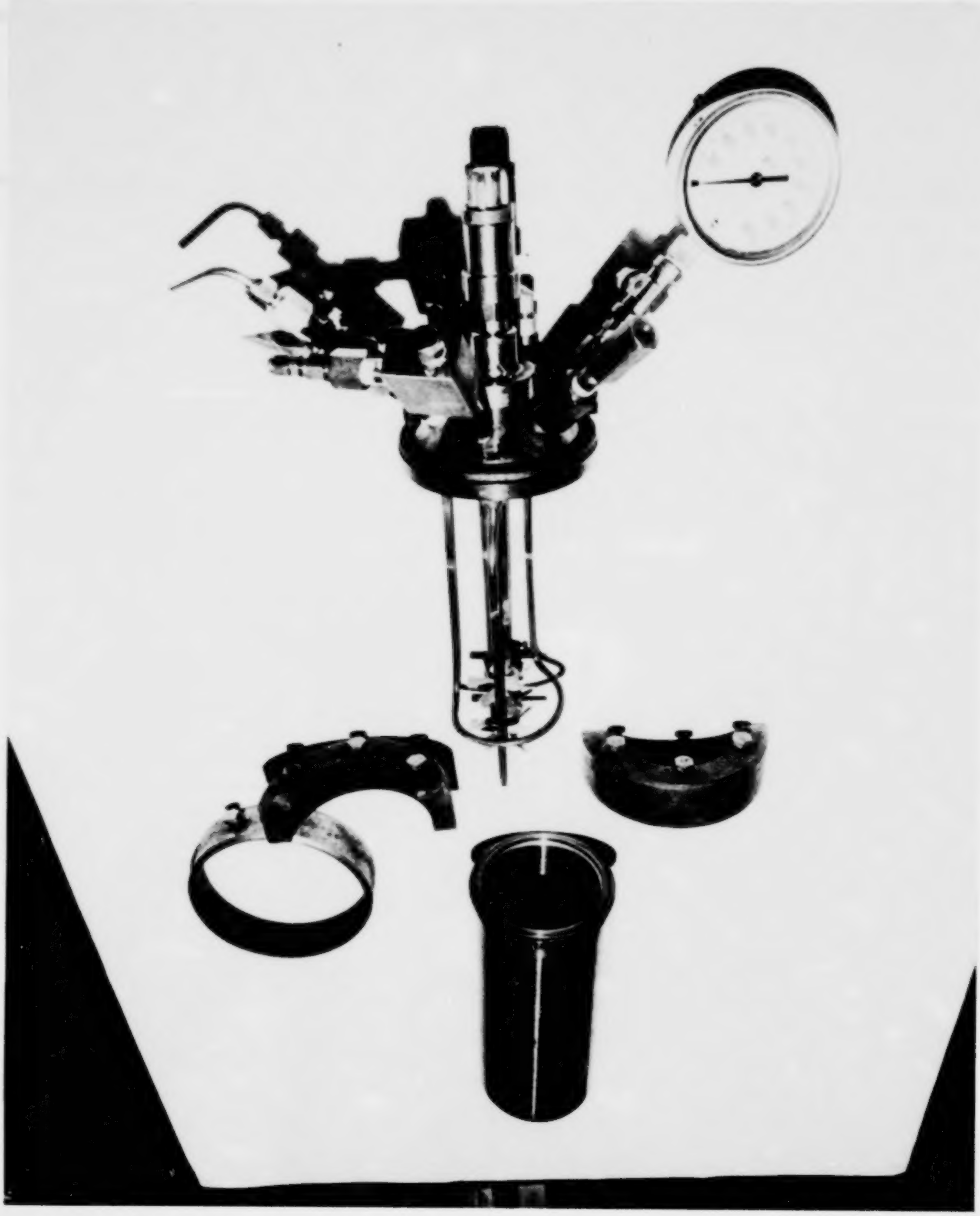


Figure 6. Photograph of Disassembled Reactor.

withdrawn during the reaction period and gas samples were taken at the conclusion of the experiment. Reactor pressure readings were obtained using a digital readout strain gauge indicator equipped with a bonded strain gauge transducer. Three Bourdon mechanical gauges were also used to monitor pressure in individual parts of the system. Temperature was monitored by an Omega Digital Readout Trendicator with an Omega Thermistor. Reactor pressure and temperature were recorded during the experiment by a dual pen strip chart recorder.

An internal quench coil used for cooling the reactor upon completion of a run was immersed in the reactor liquid. Cold tap water was passed through this coil for rapid cooling of the reactor. The liquid sampling system consisted of a liquid cooling coil connected to the reactor and to Valve 9 (Figure 4). The gas sampling system was similar to the liquid system in that it also contained a cooling coil. However, the gas sampling system incorporated a quick disconnect fitting to which the gas sample container could be attached. Three valves were required to vent the quick disconnect so that the filled sample bottle could be removed.

Liquid samples (approximately 25 ml each) were drawn at ambient temperature and pressure through the liquid sampling port controlled by valve 9. The total volume of the sample line was 10 ml. Consequently, each sample was preceeded by a purge of at least 10 ml to clear the sample line. A total of six liquid samples were taken during each run. Normal sample times were 0, 2, 5, 15, 30 and 60 minutes. Upon completion of the 60 minute reaction time, the reactor was cooled by the internal quench coil to less than 25°C and vented to the atmosphere.

Gas samples were taken under full reactor pressure but at ambient temperature through the gas sampling system shown in Figure 4. Because withdrawal of a 40 ml gas sample caused a significant drop in reactor pressure, only two gas samples were normally taken, and these were at the conclusion of the experiment. The first gas sample was taken at 60 minutes with the reactor in the hot condition, and the second sample was taken after the reactor had been cooled but before venting to the atmosphere. Each gas sample was preceeded by a purge to clear the sample line. Like the gas samples, the purges were withdrawn at reactor pressure and ambient temperature using 40 ml capacity pressure cylinders.

All of the tubing associated with the system was made of 316-stainless steel. The liquid and gas sampling lines were 3.2 mm O.D. tubing. The cooling coils consisted of single pass tube in shell devices and cooled the gas samples to ambient temperature. The gas samples were collected in 40 ml cylinders manufactured by the Whitey Company. Liquid samples were collected in 60 ml polyethylene bottles.

OZONATION: MATERIALS AND METHODS

The ozonation reactor consisted of a glass tube 2.54 cm in diameter with a liquid depth of 50 cm and total height of 61 cm. Ozone was fed through a single 1.6 mm orifice at the bottom. During typical experiments, 250 ml of aqueous solution at 25°C and initial reactant concentration of 50 mg/ℓ or 1000 mg/ℓ was contacted with 0.6 ℓ/min of ozonated air produced by a Welsbach-T-816 ozonator. The ozone concentration in the feed gas averaged 25 mg/ℓ and the mass rate of ozone fed to the reactor averaged 15.6 mg/min. Ozone in the feed and exit gas was determined by passing these streams through 2% potassium iodide traps followed by a wet test meter. During several experiments, the potassium iodide traps were alternated at 2 minute intervals so that ozone consumption could be measured as a function of time. Figure 7 shows a diagram of the ozonation system.

The mass transfer characteristics of the ozone reactor were determined by measuring the overall volumetric mass transfer coefficient, K_La, for oxygen using the nonsteady state reaeration method coupled with the exponential model and nonlinear least squares parameter estimation (29,30). This resulted in an oxygen K_La value of 1.05 min^{-1} at an air rate of 0.6 ℓ/min. The corresponding K_La value for ozone was estimated by assuming that the overall volumetric mass transfer coefficient varied as the diffusivity to the 0.5 power.

$$(K_La)_{O3} = (K_La)_{O2} \left(\frac{D_{O3}}{D_{O2}}\right)^{0.5} \qquad 4$$

where: $(K_La)_{O3}$ = overall volumetric mass transfer coefficient for ozone, t^{-1}

$(K_La)_{O2}$ = overall volumetric mass transfer coefficient for oxygen, t^{-1}

D_{O3} = diffusivity of ozone, $L^2\ t^{-1}$

D_{O2} = diffusivity of oxygen, $L^2\ t^{-1}$

At 25°C, the Wilkie-Chang relationship (31) gave 1.89 X 10^{-5} cm^2/sec for D_{O3}. The tabulated diffusivity of oxygen (31) (2.5 X 10^{-5} cm^2/sec at 20°C) was adjusted to give 2.84 X 10^{-5} cm^2/sec. Therefore $(K_La)_{O3}$ was computed to be 0.86 min^{-1} or 81% of the corresponding value for oxygen which agreed well with independent measurements (26). Gurol (26) observed a marked increased in K_La in the presence of 50 mg/ℓ of phenol in a fine bubble reactor at low pH values. However, a 50 mg/ℓ of phenol did not influence the K_La value measured in this study. Photographs were taken of the column gassed at 0.6 ℓ/min to determine (32) the surface area to volume term, a, as 0.335 cm^{-1}. This allowed the overall film transfer coefficient, K_L, to be calculated as K_La/a = 2.56 cm/min = 0.043 cm/sec.

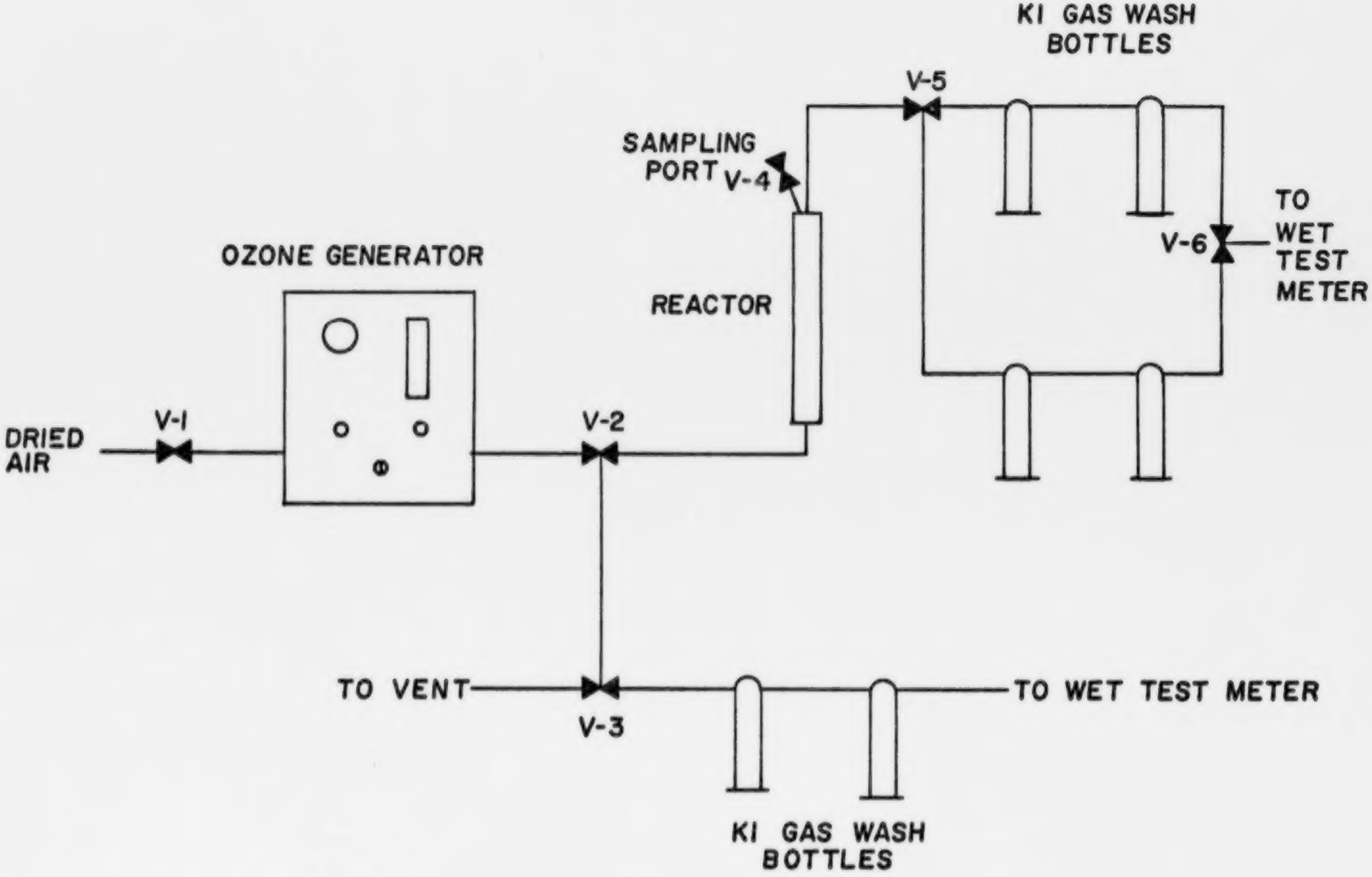

KI GAS WASH
BOTTLES
V-5
SAMPLING
PORT
V-4
TO
WET
TEST
METER
V-6
OZONE GENERATOR
REACTOR
DRIED
AIR
V-1
V-2
TO VENT
V-3
TO WET TEST METER
KI GAS WASH
BOTTLES

Figure 7. Schematic Diagram of the Experimental Ozonation System.

ANALYTICAL METHODS

Liquid Samples

Total organic carbon (TOC) was measured using a Beckman 915-B Carbon Analyzer. Chemical oxygen demand (COD) was determined by the dichromate reflux procedure outlined in Standard Methods (33). A Dionex Model 10 Ion Chromatograph was used to make the chloride measurements. 4-Nitrophenol was measured by liquid chromatography using a Hewlett-Packard 1084B liquid chromatograph (LC). The LC conditions were reverse phase, water and acetonitrile for the mobile phase, using an ODS-C18 column with a UV detector at 254 nm. The other organic reactants and oxidation products were measured by gas chromatography.

A Hewlett-Packard 5830 gas chromatograph (GC) was used to measure phenol, 2-chlorophenol, 1,2-dichloroethane and 1,2-dimethylphthalate. The columns and conditions were:

Phenol: column: Anakrom A 90/100, 5% NPGSB and 1% H_3PO_4, 1.8 m X 6.4 mm X 2 mm glass

conditions: direct injection; injection temperature, 250°C; column temperature, 235°C; gas rate, 43 ml/min; Flame Ionization Detector (FID)

2-Chlorophenol: column: H_3PO_4 treated Porapak QS, 1.8 m X 3.2 mm glass

conditions: direct injection; injection temperature, 225°C; column temperature, 240°C; gas rate, 5 ml/min; FID

1,2-Dichloroethane: column: same as 2-chlorophenol

conditions: direct injection; injection temperature, 225°C; column temperature, 185°C; gas rate, 134 ml/min; FID

1,2-Dimethylphthalate: column: Tenax GC, 60 X 80 mesh, 1.8 m X 6.4 mm

conditions: direct injection; injection temperature, 250°C; column temperature, 240°C; gas rate, 16 ml/min; FID

Wet oxidation samples were analyzed for acetaldehyde, acetone and acetic acid using the Hewlett-Packard 5830 equipment with a H_3PO_4 treated Porapak QS column. The conditions were:

direct injection; injection temperature, 250°C; column temperature, 185°C; gas rate, 23 ml/min; FID.

For certain selected wet oxidation and ozonation experiments, organic acids were measured by the procedure of Salanitro and Muirhead (34) in which the samples were subjected to a butyl esterification process. Subsequently, the butyl esters were identified and measured by gas chromatography using a Hewlett-Packard 5880 GC equipped with a SP-2100, 25 mm silica capillary column. The conditions were:

> splitless technique with valve interrupt of the purge for 30 seconds; temperature program, 40°C, 8°C/min for 5 minutes then 20°C/min to 250°C; gas rate, carrier gas (helium) at 5 ml/min, nitrogen auxiliary makeup at 30 ml/min; FID

Table 4 contains the peak retention times for the butyl esters as indicated by the chromatograms.

TABLE 4. TYPICAL PEAK RETENTION TIMES FOR BUTYL ESTERS

Butyl Ester of	Typical Peak Retention Time (min)
Formic Acid	3.85
Reagent	3.90
Acetic Acid	4.57
Reagent	5.64
Propionic Acid	5.84 (internal standard)
Butyric Acid	7.00 (reagent)
Oxalic Acid	10.55
Malonic Acid	11.20 (internal standard)
Maleic Acid	11.92
Succinic Acid	12.10
Muconic Acid	14.20

Gas Samples

The wet oxidation gas samples were analyzed for oxygen, carbon dioxide, nitrogen and carbon monoxide. Two instruments were used to perform the analysis. Some samples were analyzed by a Fisher Hamilton Model #29 Gas Partitioner while others were analyzed by a Hewlett-Packard 5830 GC. Carbon dioxide was separated on a 1.8 m X 6.4 mm aluminum column packed with 30% DEHS on 60 to 80 mesh chromosorb P while oxygen, nitrogen and carbon monoxide were separated using a 2.0 m X 4.8 mm aluminum column packed with 40 to 60 molecular sieve 13x. A thermal conductivity detector operated at $70^{\circ}C$ was used in each instrument. When the Fisher Hamilton instrument was used for analysis, the columns were installed in series and the gas sample was separated in one analysis. When the Hewlett-Packard instrument was used the gas sample had to be analyzed twice because the instrument could only handle one column at a time.

SECTION 5

OZONATION RESULTS AND DISCUSSION

EVALUATION OF AIR STRIPPING DURING OZONATION

Quantities of organic reactants removed by possible volatilization were estimated by conducting air stripping experiments under conditions identical to those of the ozonation experiments. Decreases in organic reactant concentrations indicated removal by volatilization.

Table 5 shows the results of air stripping experiments conducted at a gas rate of 0.6 ℓ/min on a liquid volume of 0.25 ℓ containing initial organic concentrations of 50 mg/ℓ. Relative concentration, defined as the ratio of the concentration to the initial concentration, did not decrease significantly for phenol, 2-chlorophenol, 4-nitrophenol and 1,2-dimethylphthalate. However, 1,2-dichloroethane showed appreciable volatility as measured relative concentration decreased by 95% during the first 30 minutes of air stripping. Because of this, no ozonation experiments were conducted using 1,2-dichloroethane. The measured relative concentrations generally agree with relative concentrations predicted by assuming a completely mixed liquid phase with the solute in the exit gas in equilibrium with the liquid (35). For this case, a mass balance for the specific substance gives:

$$V_L \frac{dC}{dt} = -GHC \qquad 5$$

where: V_L = volume of liquid in the reactor, L^3

G = volumetric gas flow rate, $L^3\ t^{-1}$

H = Henry's Law constant, defined by $H = C_g/C_a^*$, dimensionless

C_g = concentration of specific substance in the gas phase, $\underline{m}\ L^{-3}$

C_a^* = aqueous concentration of the specific substance in equilibrium with the gas phase, $\underline{m}\ L^{-3}$

Integrating gives:

$$\frac{C}{C_o} = \exp\left(-H \frac{G}{V_L} t_r\right) \qquad 6$$

TABLE 5. MEASURED AND PREDICTED RELATIVE CONCENTRATIONS DURING AIR STRIPPING

Measured Relative Concentration = $\frac{C}{C_o}$

Time (min)	Phenol	2-CP*	4-NP*	DMP*	DCE*
0	1.00	1.00	1.00	1.00	1.00
5	1.05	1.00	-	1.00	0.64
10	0.98	1.04	1.00	0.80	0.37
20	1.01	1.00	1.00	0.91	-
30	1.00	1.07	1.00	0.96	0.048
60	1.04	0.93	1.04	0.95	0.01

Predicted Relative Concentration = $\frac{C}{C_o}$

Time (min)	Phenol	2-CP	4-NP	DMP	DCE
30	0.999	0.93	0.97	0.998	0.03
60	0.998	0.87	0.93	0.997	0.0007

*	
2-CP	2-Chlorophenol
4-NP	4-Nitrophenol
DMP	1,2-Dimethylphthalate
DCE	1,2-Dichloroethane

where: C_o = aqueous concentration of specific substance at time zero $\underline{m}\ L^{-3}$

t_r = stripping time, t

For the conditions of the stripping experiments:

$$\frac{G}{V_L} = \frac{0.6\ \ell/\text{min}}{0.25\ \ell} = 2.4\ \text{min}^{-1}$$

Equation 6 was applied with the known values of Henry's constant (36) listed in Table 6 to calculate the predicted relative concentration values listed in Table 5 for times of 30 and 60 minutes. The predicted and measured concentrations are in general agreement. The assumption that the exit gas is in equilibrium with the liquid caused the predicted relative concentrations to reflect the maximum possible volatilization. In view of this and the volatilization reflected by the measured relative concentrations, it is seen that removal of specific substance by volatilization was insignificant for phenol, 4-nitrophenol and 1,2-dimethylphthalate. For 2-chlorophenol, volatilization removed a small amount (about 10%) of the solute over 60 minutes, whereas nearly all of the 1,2-dichloroethane was volatilized.

TABLE 6. VALUES OF HENRY'S CONSTANT USED TO CALCULATE PREDICTED RELATIVE CONCENTRATIONS

Substance	Henry's Constant $\left(\frac{\text{mol}/\ell\ \text{gas}}{\text{mol}/\ell\ \text{liquid}}\right)$
Phenol	1.31×10^{-5}
2-Chlorophenol	10^{-3}
4-Nitrophenol	4.68×10^{-4}
1,2-Dimethylphthalate	2×10^{-5}
1,2-Dichloroethane	5×10^{-2}

SUBSTANCE REMOVAL PATTERNS DURING OZONATION

Figures 8 through 13 show the substance and TOC removal patterns observed during ozonation of phenol, 2-chlorophenol, 4-nitrophenol and 1,2-dimethylphthalate at initial pH levels of 6 and 10. Even though the solutions contained phosphate buffer, the buffer intensity was insufficient to maintain constant pH. The initial pH values of 10 and 6 decreased to about 8 and 4.5, respectively, during ozonation. It is shown below that the rate of reaction between ozone and the primary organic substance was limited by the rate of ozone transfer. Because of this it was not possible to determine kinetic rate constants directly from the removal patterns. For purposes of comparison, the specific substance and TOC removal patterns were modelled by an empirical exponential equation:

$$\frac{C}{C_o} = \exp\,(-m_r t_r) \qquad 7$$

where: C = aqueous concentration of specific substance or TOC at time t, $\underline{m}\ L^{-3}$

C_o = aqueous concentration of specific substance or TOC at time zero, $\underline{m}\ L^{-3}$

m_r = removal parameter, t^{-1}

This empirical model was fit to the substance and TOC data by nonlinear least squares regression (30) and is shown by the curves on Figures 8 through 13. The solutions were prepared so that the initial concentrations, C_o, of specific substances were approximately 50 mg/ℓ and the samples taken at time zero showed concentrations within 10% of this value. To allow for error in C_o, best fit values of this parameter were estimated along with the best fit values of m_r by nonlinear regression. Table 7 shows the parameter estimates which resulted from fitting the empirical exponential equation to both the specific substance and TOC removal patterns. Although phenol and 4-nitrophenol showed higher values of m_r for specific substances under alkaline conditions, 2-chlorophenol yielded a greater specific substance removal parameter under acidic conditions. The TOC removal parameters for both phenol and 2-chlorophenol significantly decreased with increasing pH. However, at a given pH range, the TOC removal parameters of various phenolic compounds were similar. This suggests similarities between the intermediate substances formed during ozonation of the various phenolic compounds.

Caution should be used in attempting to make inferences regarding reaction kinetics from the substance rate parameters. In modelling similar data, Gurol (26) reported that the reactant disappearance profile was relatively insensitive to the kinetic rate constant and depended primarily on the reactor $K_L a$ value. The intermediate product profiles were more sensitive to the kinetic rate constants.

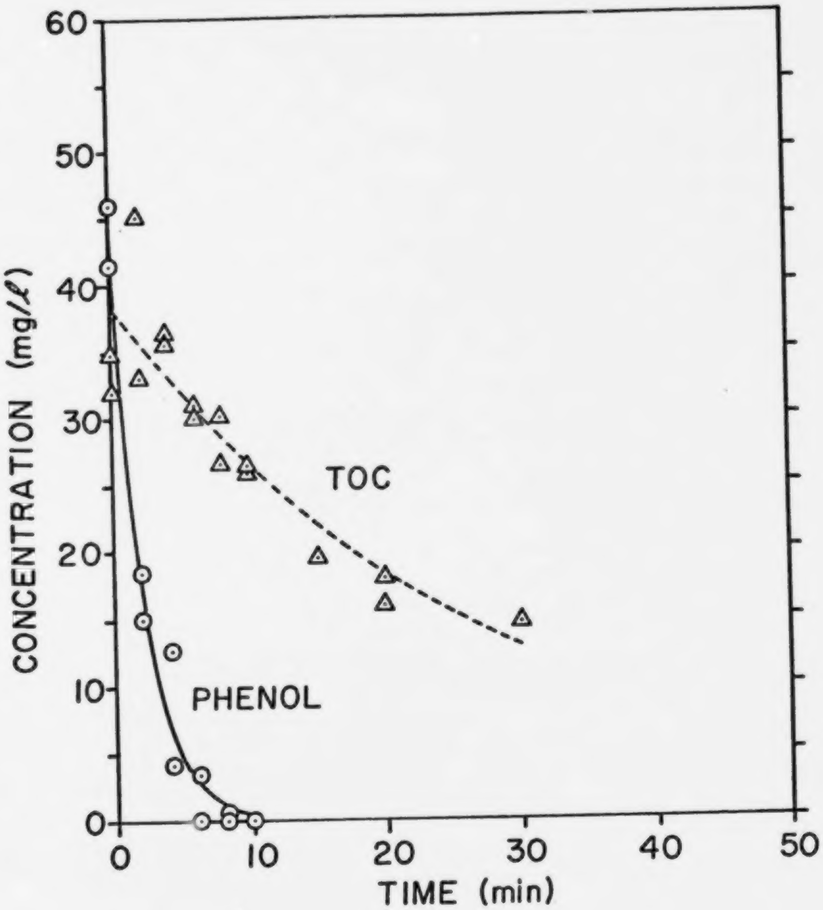


Figure 8. Phenol and TOC Destruction During Ozonation at pH 6.

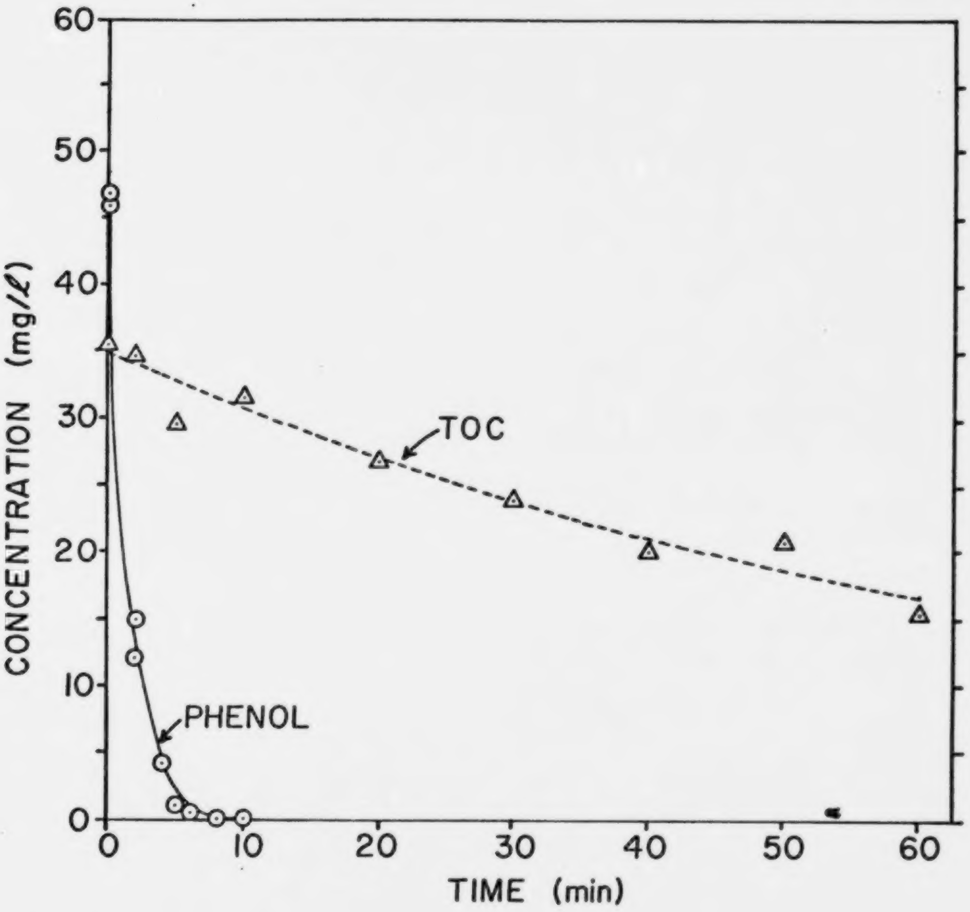


Figure 9. Phenol and TOC Destruction During Ozonation at pH 10.

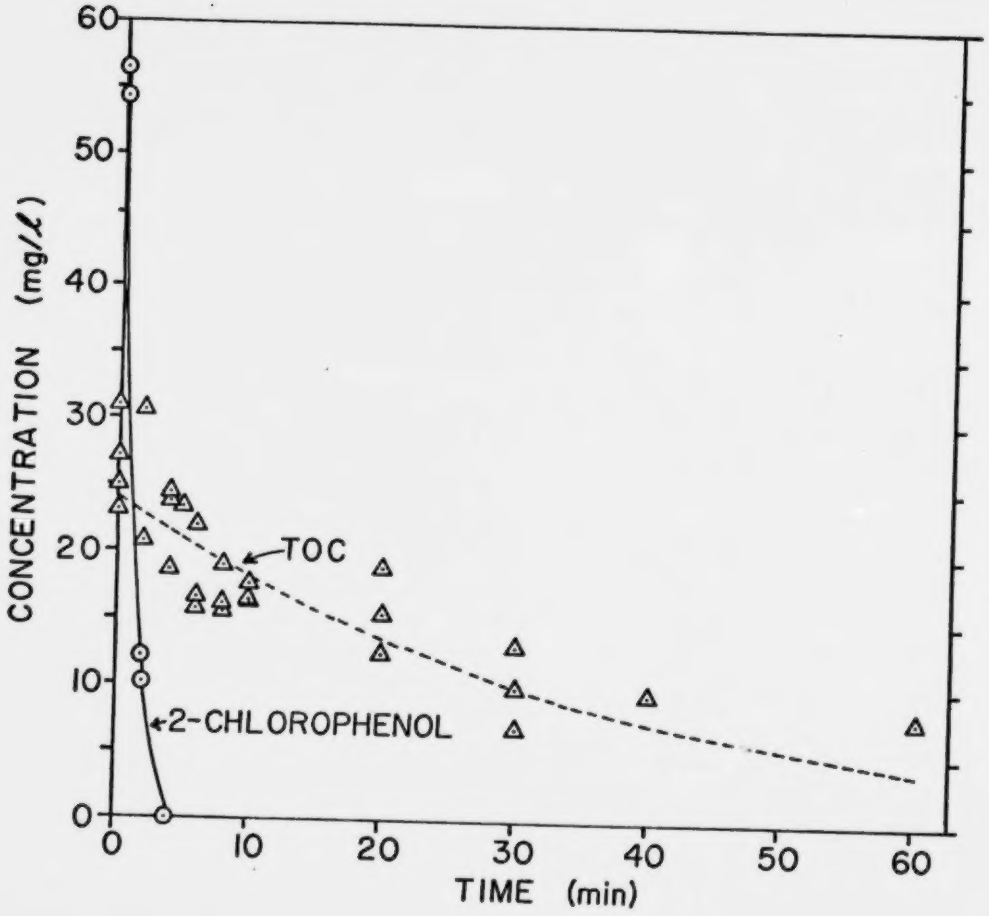


Figure 10. 2-Chlorophenol and TOC Destruction During Ozonation at pH 6.

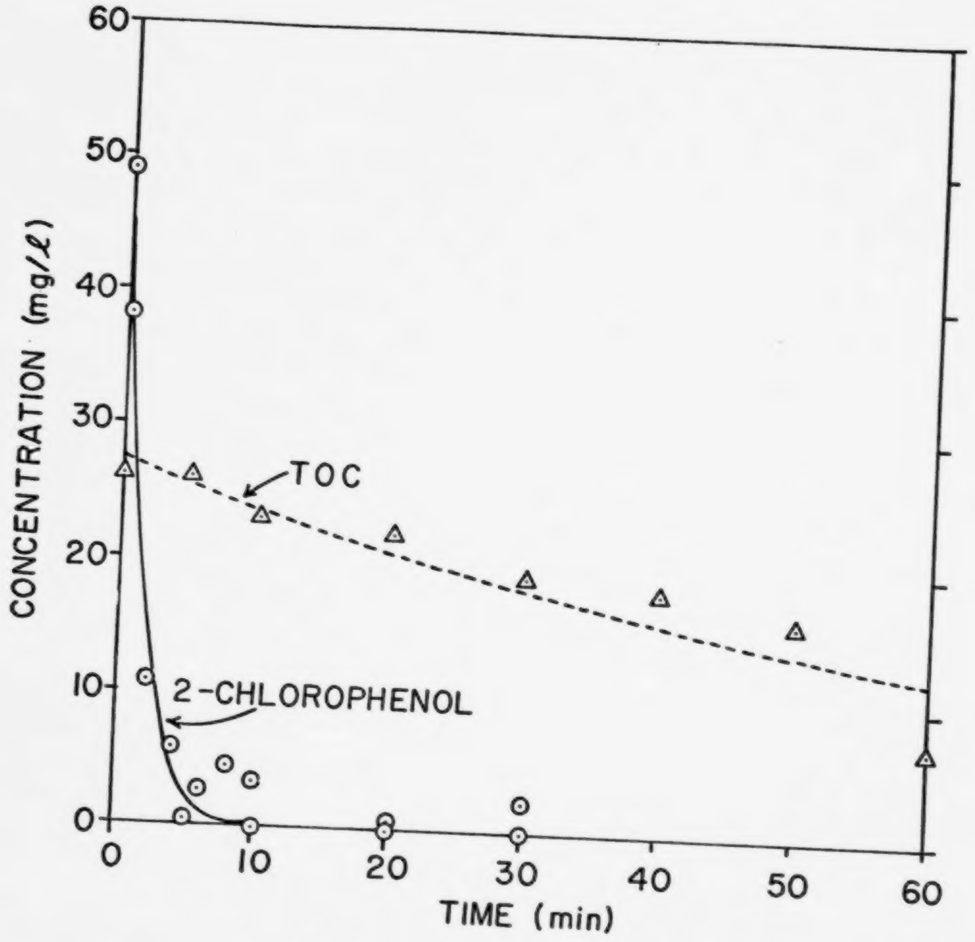


Figure 11. 2-Chlorophenol and TOC Destruction During Ozonation at pH 10.

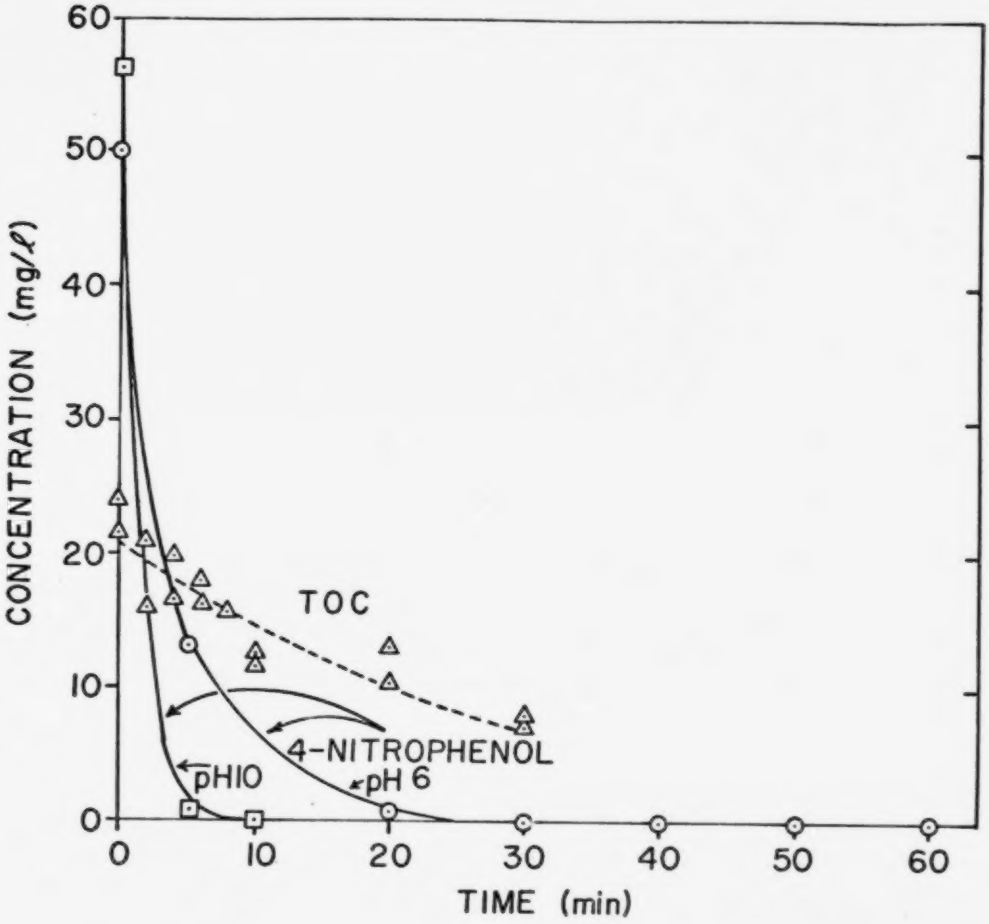


Figure 12. 4-Nitrophenol and TOC Destruction at pH 6 and 4-Nitrophenol Destruction at pH 10 During Ozonation.

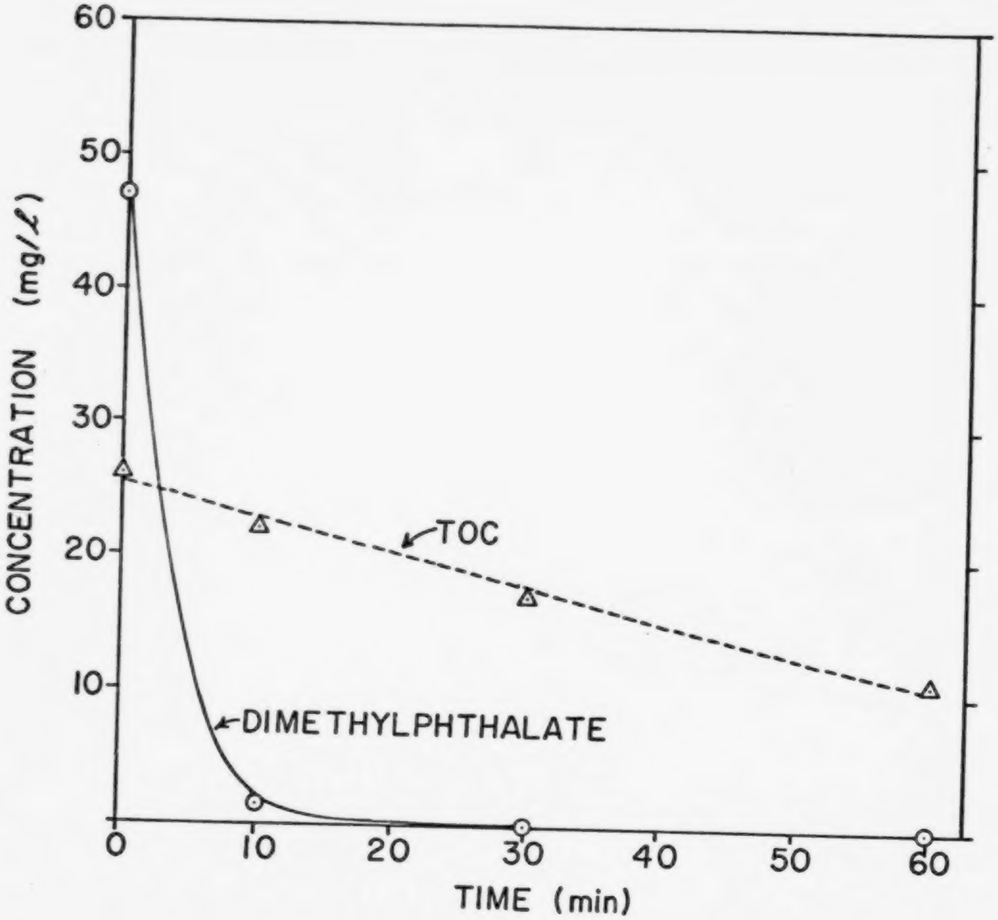


Figure 13. Dimethylphthalate and TOC Destruction During Ozonation at pH 6.

TABLE 7. PARAMETER ESTIMATES FOR SPECIFIC SUBSTANCE AND TOTAL ORGANIC CARBON REMOVAL PATTERNS

	Phenol		2-CP		4-NP		DMP
Initial pH	6	10	6	10	6	10	6
Specific Substance							
Nominal C_o (mg/ℓ)	50	50	50	50	50	50	50
Estimated C_o (mg/ℓ)	44	46	55	43	50	56	47
Estimated Removal parameter, $m_r (min^{-1})$	0.46	0.62	0.83	0.61	0.26	0.84	0.35
Total Organic Carbon							
Nominal C_o (mg/ℓ)	38	38	28	28	26	26	31
Estimated C_o (mg/ℓ)	38	35	25	27	21	-	26
Estimated removal parameter, $m_r \times 10^2$ (min^{-1})	3.7	1.2	3.0	1.4	3.7	-	1.3

OZONE CONSUMPTION

During several ozonation experiments, the potassium iodide trap through which the reactor exhaust passed was changed at intervals of 2 to 10 minutes. In this way, the average mass rate of ozone leaving the reactor could be calculated for each time interval. The mass rate of ozone fed to the reactor was known from measurements made before and after the experiment. Therefore, the ozone utilization profile during the experiment could be determined by difference. During the first two minutes of reaction, approximately 40 to 70 percent of the ozone supplied was utilized. However, this percentage decreased rapidly after four minutes so that, during the period of 10 to 30 minutes the ozone utilized was on the order of five percent of the amount fed. Therefore, precise determination of ozone utilization could be determined only for the first few minutes of reaction. Table 8 compares the initial rates of ozone and specific substance utilization for various experiments in which ozone utilization profiles were measured. The specific substance mass utilization rate, R_s, was calculated as:

$$R_s = V_L \left(\frac{\Delta C}{\Delta t}\right) = V_L \left(\frac{C_o}{\Delta t}\right)(1 - \exp(-m_r t_r)) \qquad 8$$

where Δt is evaluated as the difference between concentrations at time t and time zero predicted by the empirical exponential model which had been fit to the data. The initial utilization ratio was calculated as:

$$\frac{\text{moles ozone used}}{\text{mole substance used}} = \frac{R_o\,(MW_s)}{R_s\,(MW_o)} \qquad 9$$

where: R_o = mass utilization rate of ozone, $\underline{m}\ t^{-1}$

MW_s = molecular weight of specific substance, $\underline{m}\ \text{mol}^{-1}$

MW_o = molecular weight of oxygen, $\underline{m}\ \text{mol}^{-1}$

The value of the initial utilization ratio for phenolic compounds (3.9 to 5.9 moles/mole) is consistent with similar ratios observed by others. Eisenhauer (27) measured an ozone utilization of 3 to 4 moles of ozone per mole of phenol. Gilbert (37) studied the ozonolysis of mono-, di-, and trichlorophenols and reported an ozone consumption of 3.2 to 5 moles of ozone per mole of chlorophenol. Others (25,38) stated that phenolic compounds react with 3 moles of ozone per mole of compound to break the olefinic bonds. In this study, it appears that values of the utilization ratio greater than 3.0 were caused by ozone decomposition at the slightly acidic and alkaline pH condition and by possible reaction of ozone with organic intermediates (e.g. formic acid) produced by the initial reactions of ozone and phenolic compound.

TABLE 8. INITIAL RATES OF OZONE AND REACTANT UTILIZATION

Substance	Initial pH	Initial Utilization Rates (0 to 2 min.) Ozone, R_o (mg/min)	Initial Utilization Rates (0 to 2 min.) Substance, R_s (mg/min)	Initial Utilization Ratio (mol ozone/mol substance)	Apparent Enhancement Factor
Phenol	6	6.6	3.3	3.9	3.3
2-Chlorophenol	6	10.1	5.6	4.8	5.0
2-Chlorophenol	10	8.3	3.8	5.9	4.1
4-Nitrophenol	6	5.4	2.5	5.9	2.7
4-Nitrophenol	6	5.3	2.5	5.8	2.6
1,2-Dimethylphthalate	10	3.7	-	-	1.9

ENHANCEMENT OF MASS TRANSFER BY SIMULTANEOUS DIFFUSION AND REACTION OF OZONE

Others (26,39) have observed that, during ozonation of certain organic substances under semi-batch conditions, the concentration of dissolved ozone remains undetectable in the bulk liquid until the concentration of the organic substance decreases close to zero. Although dissolved ozone was not measured in this study, it is suspected that the dissolved ozone concentration remained close to zero until the initial organic substance had disappeared. Under these conditions, it is possible for the reaction in the diffusive film to increase the concentration gradient of ozone and thereby enhance mass transfer. For the case of a second order reaction between a diffusing dissolved gas, A, and a dissolved substance, B, such as that between ozone and dissolved organics:

$$A_{(O_3)} + zB_{(org)} \xrightarrow{k_o'} \text{products} \qquad 10$$

Dankwerts (40) has shown that the amount of diffusing gas which reacts in the film will be negligible in comparison to that which reacts in the bulk liquid if:

$$\frac{D_A\,(k_o')\,(C_B)}{K_L^{\,2}} \ll 1 \ll \frac{k_o'\,(C_B)}{K_L a} \qquad 11$$

where: D_A = diffusivity of the diffusing gas, $L^2\ t^{-1}$

k_o' = second order rate constant, mol $L^{-3}\ t^{-1}$ ($k_o'C_BO_3$ = moles A/time)

C_B = concentration of dissolved substance in the bulk liquid, $\underline{m}\ L^{-3}$

If this condition is not met, a significant fraction of the diffusing gas will react in the film and this simultaneous diffusion and reaction will cause the rate of mass transfer to be enhanced by a factor E, the enhancement factor, given approximately by (40):

$$E = \frac{\left[M\,\dfrac{E_i - E}{E_i - 1}\right]^{0.5}}{\tanh\left[M\,\dfrac{E_i - E}{E_i - 1}\right]^{0.5}} \qquad 12$$

where: $M = D_A (k_o')(C_B)/K_L^2$, dimensionless

$$E_i = 1 + \frac{D_B (C_B)}{z(D_A)(C_A^*)} \quad \text{, dimensionless}$$

D_B = diffusivity of the dissolved substance, $L^2\ t^{-1}$

C_A^* = equilibrium concentration of the diffusing gas in the liquid, $\underline{m}\ L^{-3}$

The maximal ozone transfer rate, W, based on the $K_L a$ value measured for ozone in the absence of reaction is determined by:

$$W = (K_L a)\ (V_L)\ (C^*_{O3}) \qquad 13$$

where: C^*_{O3} = equilibirum concentration of ozone in the liquid, $\underline{m}\ L^{-3}$

The ozone content of the gas stream was typically 25 mg/ℓ. Based on this value, and a solubility coefficient of 0.37 mg/ℓ in liquid per mg/ℓ in gas (26) at 25°C, C^*_{O3} is calculated as 9.25 mg/ℓ, and the maximal transfer rate in the absence of reaction is:

$$(0.86\ \text{min}^{-1})\ (0.25\ \ell)\ (9.25\ \text{mg}/\ell) = 2.0\ \text{mg/min}$$

This is clearly less than the measured ozone utilization rates listed in Table 8 indicating an apparent enhancement of the transfer rate in the presence of reaction. The apparent enhancement factors listed in Table 8 were calculated by dividing the measured initial ozone utilization rate by the maximal transfer rate in the absence of reaction, 2.0 mg/min.

It has been reported (26) that the reaction rate of constants for ozonation of phenol and phenolate are 1.1×10^3 and 4×10^7 ℓ/mol·sec, respectively. Because the pK of phenol (corrected for ionic strength of 0.15) is 9.6, the reaction rate would be expected to increase markedly as the pH increased above 6.

At pH values of 6.6, 7.6, 8.6 and 9.6, the total phenolic concentration present as phenolate ion would be 0.1%, 1%, 10% and 50%, respectively. Assuming that ozone is used only by direct reaction with phenol and phenolate, Equation 12 can be evaluated for the conditions prevailing during the first two minutes of the ozonation experiments, where the total phenolic concentration was roughly 40 mg/ℓ. The results of this calculation are shown in Table 9 and, at pH 6, indicate an enhancement factor of only 1.06, considerably lower than the value of 3.3 measured for phenol at pH 6. Based on this, it appears that ozone decomposition or reaction with intermediate products may cause E to be greater than predicted by considering reaction with only phenol and phenolate.

TABLE 9. CALCULATED VALUES OF THE ENHANCEMENT FACTOR ASSUMING THAT OZONE IS USED ONLY BY REACTION WITH PHENOL AND PHENOLATE.

pH	$\frac{D_A k_o' C_B}{K_L^2}$	E
6.6	0.18	1.06
7.6	1.75	1.45
8.6	17.5	2.9
9.6	87.4	4.05
10.6	175	4.35

calculations based upon Equation 12 with

$K_L = 0.043$ cm/sec

$D_{phenol} = 10^{-5}$ cm^2/sec

$D_{ozone} = 1.9 \times 10^{-5}$ cm^2/sec

$z = 1/3$

$C_A^* = 9.25$ mg/ℓ

$E_i = 4.81$

ORGANIC CARBON TRANSFORMATIONS DURING OZONATION

Figures 14 and 15 show organic acid profiles during ozonation of 50 mg/ℓ phenol and 1000 mg/ℓ 2-chlorophenol respectively. In both cases, formic and oxalic acids were observed to be important intermediate and end products. Total oxygen carbon (TOC) measurements indicated that, for phenol at 50 mg/ℓ, the acids measured accounted for 60 to 80 percent of the organic carbon present. However, for 2-chlorophenol at 1000 mg/ℓ, the acids measured only accounted for 26 to 42 percent of the organic carbon measured. The remaining portion of the organic carbon presumably consisted of substances other than organic acids.

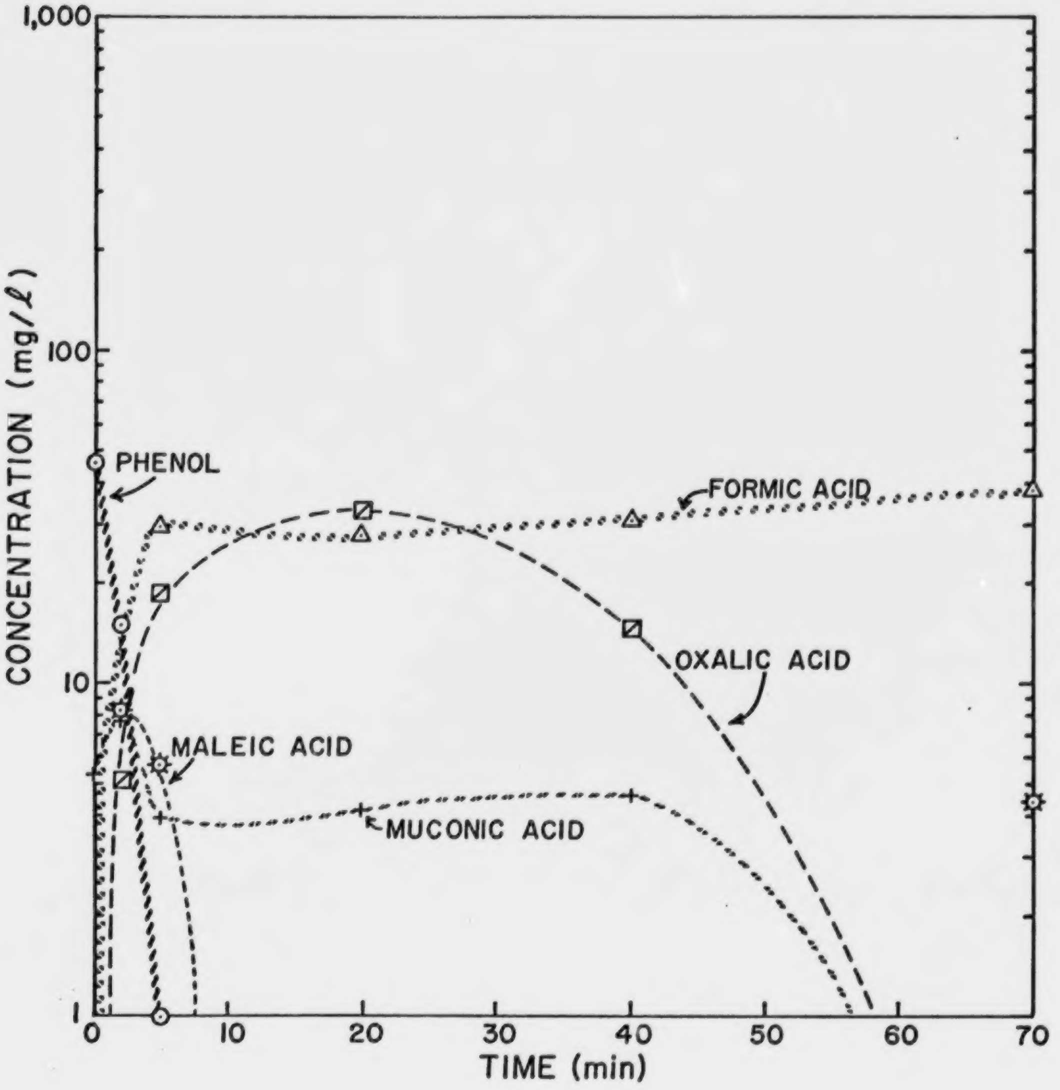


Figure 14. Organic Acid Profiles During Ozonation of Phenol at pH 10.

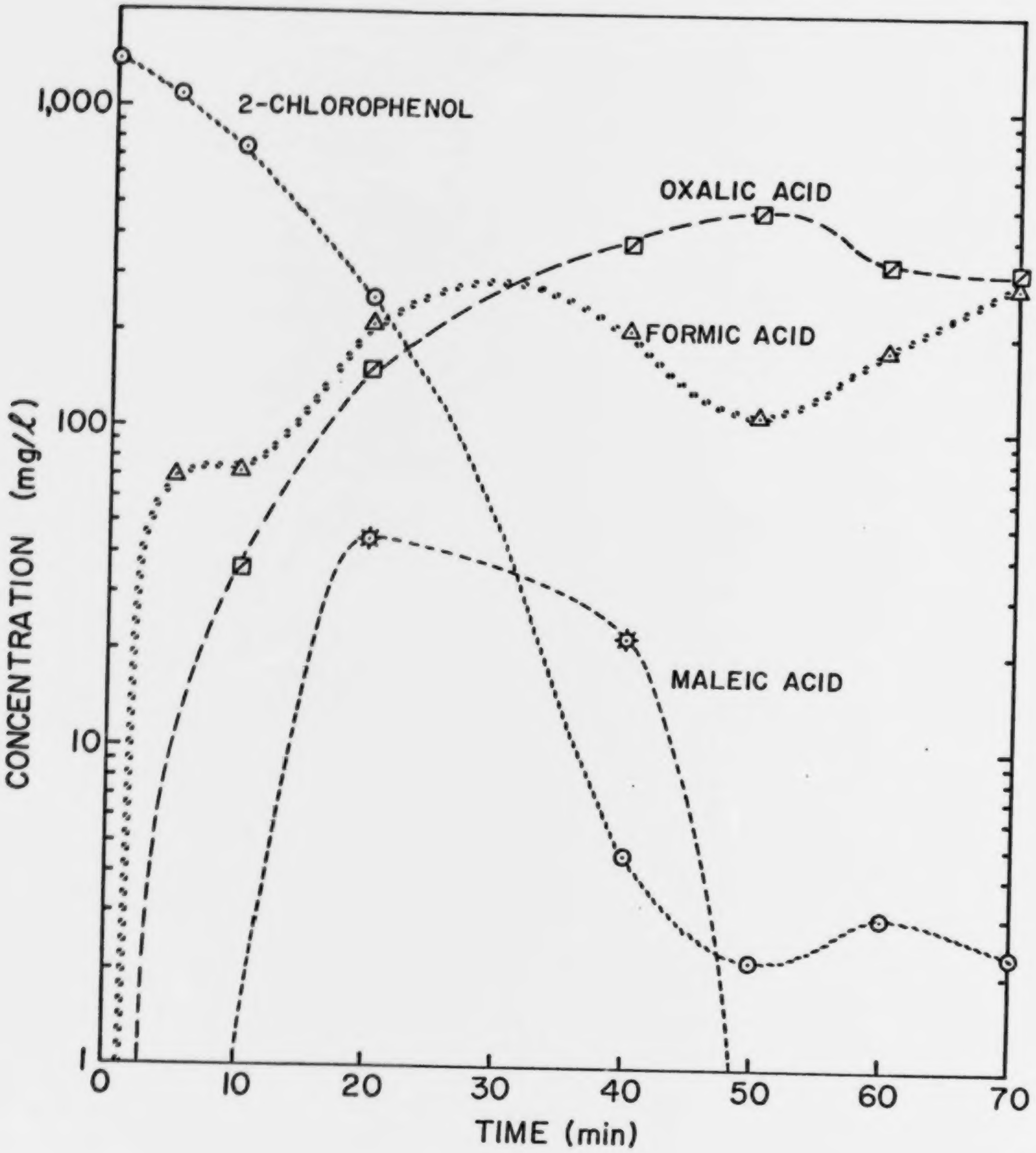


Figure 15. Organic Acid Profiles During Ozonation of 2-Chlorophenol at pH 10.

Aldehydes were not measured and could have accounted for much of the remaining organic carbon. In addition to the four acids shown in Figures 14 and 15, (formic, oxalic, muconic, and maleic) standards were run for acetic and succinic acids, but these acids were not detected in the ozonated samples. Various additional peaks were detected on the chromatograms of the esterified samples, but were not identified. Two of these at retention times of 4.63 and 10.61 minutes were consistently present. These were not identified, but, based on relative retention times, the 4.63 minute peak could have been glycolic, glyoxylic, or pyruvic acids. Although catechol and hydroquinone were expected from phenol, they were not found, presumably because they could have been present very early in the reaction and been missed or they could have been present at concentrations below the detection limit.

Comparison of Figure 14 to similar data obtained for phenol by Yamamoto et al. (14) indicates a substantially faster rate of phenol utilization and acid production in this study, presumably because of a higher ozone dosage rate. Similar concentrations of formic and oxalic acids were observed in each study. The decrease in oxalic acid concentration in the presence of formic acid indicated in Figure 14 at times greater than 40 minutes was not observed by Yamamoto et al. This might be attributable to differences in pH values, dosage rates and temperatures between the two studies.

SECTION 6

WET OXIDATION RESULTS AND DISCUSSION

For each experiment, the measured raw data consisted basically of time profiles of liquid phase concentration, temperature and pressure during the course of the wet oxidation reaction. In addition, gas phase concentrations of oxygen, nitrogen, carbon monoxide and carbon dioxide were measured at the conclusion of each experiment. These data were subjected to the following analyses:

> Material Balances: The amount of carbon, oxygen and chlorine recovered at the conclusion of each experiment were compared to the amounts injected. Considering the precision of the measurements, a percent recovery within 15% of the theoretical 100% was taken as desirable in the absence of other explanations. Unexplained deviation by more than this amount cast doubt on the accuracy of the data.
>
> Kinetic Analysis: The rates of removal of the specific substance, COD and TOC were modeled by various first-order models. The kinetic parameters were then compared to determine the influence of the control variables (temperature, initial pH and copper catalyst).
>
> Product Analysis: Although no attempt was made to mathematically describe the rates of final and intermediate product formation, the substances formed were examined and compared with the independent carbon measurements and with data reported by others.

MATERIAL BALANCES

Carbon Balance

The carbon balance was made on a cold (ambient temperature) basis and is reported in terms of percent carbon recovery, given by:

$$\%\ \text{Carbon Recovery} = \left[\frac{C_{ils} + C_{ols} + C_{igs} + C_{ogs} + C_{of} + C_{ifg} + C_{ifl}}{C_t}\right] 100 \qquad 14$$

where: C_{ils} = inorganic carbon removed by liquid sample and purges, m

C_{ols} = organic carbon removed by liquid samples and purges, m

C_{igs} = inorganic carbon in gas samples and purges, m

C_{ogs} = organic carbon in gas samples and purges, m

C_{of} = organic carbon in final liquid inventory, m

C_{ifg} = inorganic carbon in final gas inventory, m

C_{ifl} = inorganic carbon in final liquid inventory, m

C_t = total carbon injected, m

The procedure used to evaluate each of these terms is given in Appendix A along with a numerical example. It was determined that the C_{ils} and C_{ogs} terms were negligible and could be neglected in the balance. This was because the bulk of the liquid samples were taken early in the run before appreciable carbon dioxide had been generated and the gas samples were taken at the conclusion of the run when the concentration of volatile materials was low.

An earlier report (9) indicated that a significant fraction of the final organic carbon inventory would exist in the vapor phase. However, if this were the case, the liquid phase organic concentrations would have increased as the reactor cooled. A "t" test on all the measured parameters for the 2-chlorophenol, 4-nitrophenol, 1,2-dimethylphthalate and 1,2-dichloroethane experiments showed no significant difference between the final 60 minute hot samples and the cool reactor liquid content samples.

Evaluation of the C_t, C_{ols}, C_{igs}, C_{of}, and C_{ifg} terms was straightforward and based on the experimental measurements and analyses. However, calculation of the C_{ifl} term was based on the assumption that the measured carbon dioxide concentration in the gas phase was in equilibrium with carbonic acid according to Henry's Law. Carbonic acid in turn was assumed to be in equilibrium with bicarbonate and carbonate. Calculation of gas phase quantities was based on the ideal gas law at ambient temperatures.

The results of the carbon balances for 2-chlorophenol are given in Table 10. The mean carbon recovery for all experiments was 112% and the 95% confidence limits of the mean ranged from 98% to 126%. Similar tables for each substance are found in Appendix B. The results of the carbon balances for each substance are summarized in Table 11. The mean carbon recovery varied from 85% for 1,2-dimethylphthalate to 114% for 4-nitrophenol.

Table 12 shows a detailed breakdown of material balance data for 2-chlorophenol. A general trend can be seen that, with increasing temperature, there was a decrease in organic carbon in the final inventory. Similar tables for each substance are presented in Appendix B.

TABLE 10. 2-CHLOROPHENOL MATERIAL BALANCE RESULTS

Experiment	Conditions	Percent Recovery		
		Carbon	Oxygen	Chlorine
12	204°C	112	116[a]	97
13	204°C	108	104	97
14	232°C	93	134[a]	101
15	232°C	90	114	47
16	260°C	147	133	94
17	260°C	94	125	93
18	204°C, High pH	147	159[a]	85
19	232°C, High pH	133	261[a]	97
20	204°C, Copper Catalyst	93	131[a]	103
21	232°C, Copper Catalyst	106	119	102
	Mean	112	129	92
	95% C.L.*	98-126	96-162	82-101

[a] Calculated using headspace parameters of reactor at operating temperature; all others using injection system parameters.

* Mean 95% confidence limit.

TABLE 11. SUMMARY OF MATERIAL BALANCE RESULTS

Substance	Percent Recovery (Mean 95% Confidence Limits)		
	Carbon	Oxygen	Chlorine
Phenol	104 (89-119)	143 (115-170)	- -
2-Chlorophenol	112 (98-126)	129 (96-162)	92 (82-101)
4-Nitrophenol	114	105	-
1,2-Dimethylphthalate	85 (73-96)	104 (91-117)	- -
1,2-Dichloroethane	94 (84-105)	88 (69-107)	90 (83-97)

Oxygen Balance

The oxygen balance was made on a cold basis and compared the initial inventory of molecular oxygen with an allowance for the amount of molecular oxygen used to accomplish the COD reduction. The results are given in terms of percent oxygen recovery, defined by:

$$\%\ \text{Oxygen Recovery} = \left[\frac{O_{ls} + O_{gs} + O_{fg} + O_{fl} + COD_u}{O_t}\right] 100 \qquad 15$$

where: O_{ls} = oxygen removed with liquid samples and purges, m

O_{gs} = oxygen removed by gas samples and purges, m

O_{fg} = oxygen in final gas inventory, m

O_{fl} = oxygen in final liquid inventory, m

COD_u = oxygen used to accomplish reduction in COD, m

O_t = total oxygen present after injection, m

TABLE 12. 2-CHLOROPHENOL MATERIAL BALANCE BREAKDOWN

Experiment	C_t (g)	C_{ols} (g)	C_{of} (g)	C_{igs} (g)	$C_{ifg} + C_{ifl}$ (g)	% Rec'd	O_t (g)	O_{gs} (g)	$O_{fl} + O_{fg}$ (g)	COD_u (g)	% Rec'd
12	2.800	0.444	0.919	0.354	1.430	112.4	13.493[a]	3.490	10.302	1.843	115.9
13	2.800	0.371	1.179	0.318	1.147	107.6	18.724	3.688	11.316	4.390	103.6
14	2.800	0.494	0.448	0.328	1.337	93.1	11.888[a]	3.122	6.795	6.057	134.4
15	2.800	0.452	0.541	0.334	1.202	90.2	19.765	4.882	11.673	5.934	113.8
16	2.800	0.210	0.324	0.970	2.623	147.4	17.871	5.289	11.342	7.050	132.5
17	2.800	0.227	0.230	0.882	1.296	94.1	14.026	4.404	6.073	7.016	124.7
18	2.800	0.752	0.871	0.235	2.264	147.2	9.137[a]	2.272	7.601	4.645	158.9
19	2.800	0.787	0.915	0.355	1.666	133.0	8.603[a]	4.426	13.027	5.013	261.1
20	2.800	0.295	0.446	0.351	1.508	92.8	16.149[a]	3.495	11.178	6.458	130.8
21	2.800	0.142	0.143	0.715	1.976	106.3	15.485	3.405	7.566	7.527	119.5

[a] Calculated using headspace parameters of reactor at operating temperature; all others using injection system parameters.

Appendix A gives the procedure used to evaluate each term along with a numerical example. It was found that the O_{ls} term was small and could be neglected in the balances.

Table 10 shows the results of the oxygen balances for 2-chlorophenol. The mean recovery was 129% and the 95% confidence limits of the mean ranged from 96% to 162%. Similar tables for each substance are found in Appendix B.

Chlorine Balance

The chlorine material balance was based on the assumption that chlorine would remain bound in the 2-chlorophenol or 1,2-dichloroethane molecule or appear as chloride in the liquid phase. The results are reported as percent chlorine recovery defined by:

$$\%\ \text{Chlorine Recovery} = \left[\frac{L_{fl} + L_{ls} + L_{lss}}{L_t}\right] 100 \qquad 16$$

where: L_{fl} = chlorine in final liquid inventory, m

L_{ls} = chlorine removed in liquid samples and purges, m

L_{lss} = chlorine removed by liquid samples and purges containing initial reactant, m

L_t = total chlorine injected, m

Appendix A gives the procedure used to evaluate each term along with a numerical example.

The results of the oxygen balances for each substance are summarized in Table 11. The mean recovery ranged from 88% for 1,2-dichloroethane to 143% for phenol. The majority of the oxygen recoveries were over 100%. This suggests the presence of a systematic error in the accounting procedure. There are several features of the experimental and calculation procedures which might introduce small systematic errors of this type. Many of the calculations were based on the ideal gas law applied at the ambient temperature, but the exact temperature of the gases in the injection and sampling systems was not determined. Also, the quantities of oxygen dissolved in the liquid phase were based on literature values of Henry's constant for oxygen. Excessively high oxygen recoveries could have also been partly caused by a leaky valve in the injection system (Valve 2, Figure 4). Upon injection, the injection system and the reactor were at equal pressures. However, the leaky valve increased the injection system pressure by 10 to 30 psig over the next 5 minutes. This higher pressure was then used to calculate the amount remaining in the injection system. This, in turn caused the calculated quantity injected to be low and underestimated O_t.

WET OXIDATION SUBSTANCE REMOVAL PATTERNS

Models Applied to Describe Substance Removal Patterns in Batch Wet Oxidation

In this study, three simple models were applied to describe substance removal patterns during batch wet oxidation. These models were useful for making comparisons and are partly empirical in the sense that they do not properly account for the influence of oxygen partial pressure and possible mass transfer limitations.

The models applied were: first order, modified first order, and phasic model. The basic differential and integrated forms of the model equations are given below.

First Order

$$\frac{dC}{dt} = -m_1 C \qquad 17$$

$$C = C_o \exp(-m_1 t_r) \qquad 18$$

Modified First Order

$$\frac{dC}{dt} = -m_2 (C - C^*) \qquad 19$$

$$C = C^* + (C_o - C^*) \exp(-m_2 t_r) \qquad 20$$

Phasic

Initial Fast Reaction

$$\frac{dC}{dt} = -m_f C \qquad 21$$

$$C = C_o \exp(-m_f t_r) \qquad 22$$

Subsequent Slow Reaction

$$\frac{dC}{dt} = -m_s C \qquad 23$$

$$C = C_{tr} \exp(-m_s(t_r - t_{tr})) \qquad 24$$

where: C^* = aqueous residual concentration of substance, TOC or COD approached asymptotically as time approaches infinity, $\underline{m}\ L^{-3}$

C_{tr} = aqueous concentration of substance, TOC or COD at which the transition from the fast to slow reaction occurs, $\underline{m}\ L^{-3}$

t_{tr} = time at which the transition from the fast to slow reaction occurs, t

m_1, m_2, m_f, m_s = removal parameters for the first order, modified first order, phasic fast and phasic slow models respectively, t^{-1}

The first order model is based on conventional first order kinetics applied over the entire reaction period. For a good fit, it requires that C asymptotically approach zero. Because of this, it worked well for specific substances but was not well-suited to describing the disappearance of TOC or COD. The modified first order model is first order with respect to degradable parameters and was applied over the entire reaction period. This model was well-suited to describing the disappearance of TOC and COD because it did not require that C approach zero at infinite time. The phasic model is based on first order kinetics applied to the data in two separate stages, a first reaction period (data points at 0, 2 and 5 minutes) and a slow reaction period (data points at 15, 30 and 60 minutes). This model was applied to describe the disappearance of specific substance and TOC with primary emphasis placed on the fast reaction phase.

Parameter Estimation

The parameters contained in the integrated form of each model are summarized below:

Model	Parameters	Total Number of Parameters
First Order	C_o, m_1	2
Modified First Order	C_o, C^*, m_2	3
Phasic	C_o, m_f, C_{tr}, m_s	4

For each of the models, there are certain parameters, such as the removal parameters, which must be estimated from the model applied to the data. In addition, there are parameters such as the initial concentration for which either values estimated from the model or individual measured values could be used. For these parameters, it is better to estimate the parameters from the model rather than to use a single measured value. This is because the experimental error inherent in any single measured value would unduly bias the estimates of the other parameters (41). Therefore, in this research the various models were fit to the data by estimating all parameters from the data.

In fitting the models to the data either the differential, logarithmic or exponential forms of the model equations could be used. The differential and logarithmic forms lend themselves well to simple graphical parameter estimation procedures. However, these procedures are generally not well-suited to the estimation of more than one parameter. Furthermore, the differential and logarithmic transformation required can bias the parameter estimates. In this study, the exponential form of the model equations were fit to the data by nonlinear regression (30). The best parameter estimates were taken as those producing the minimum sum of squares of the residuals. Here a residual refers to the difference between the concentration predicted by the model and the measured concentration. In addition to giving the least squares estimates of the parameter, the nonlinear regression technique provided estimates of the standard error for each parameter. Using this information, the precision of the parameter estimates could be judged.

Influence of Temperature on Removal Patterns

Figures 16 to 20 show the removal patterns for phenol, 2-chlorophenol, 4-nitrophenol, 1,2-dimethylphthalate and 1,2-dichloroethane measured at temperatures of 204°C, 232°C and 260°C, respectively under conditions of no pH adjustment (initial pH approximately 4.5). The smooth curves in these figures represent the first order model fitted to the data by nonlinear regression. It is evident that the simple first order model adequately describes the substance removal data and that the removal increased substantially with increasing temperature. Table 13 shows the first order removal parameters for the various substances at the three test temperatures along with the approximate standard error, s, estimated for these parameters (42). The standard error values indicate a precision on the order of 10% and this was typical of the precision with which removal parameters were estimated by the various models. The estimated values of the initial concentration, C_o, were typically within 5% of the initial concentration calculated based on the quantity of substance injected. Table 14 shows the removal parameters estimated from the phasic model for the initial fast reaction. Comparison of these with the first order removal parameters shown in Table 13 show that, for most substances the removal parameters estimated based on the initial fast rate were close to those estimated from the first order model.

Interpretation of these data in light of the second order kinetics given by Equation 3 requires consideration of:

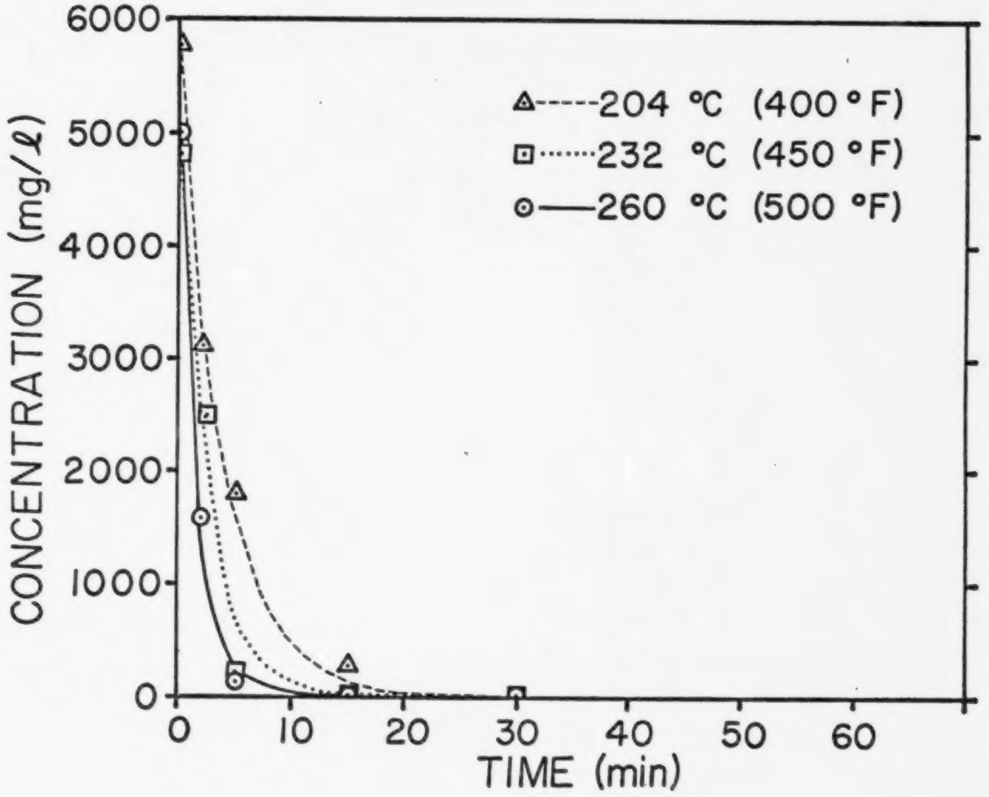


Figure 16. Influence of Temperature on Phenol Destruction During Wet Oxidation.

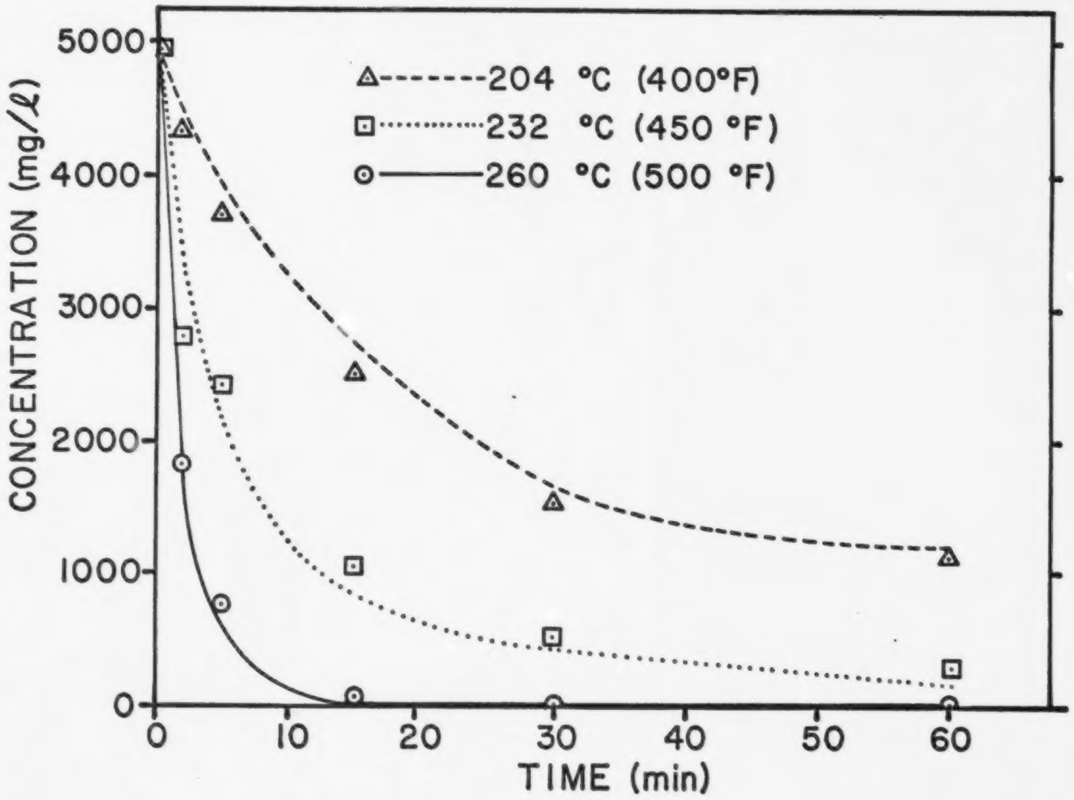


Figure 17. Influence of Temperature on 2-Chlorophenol Destruction During Wet Oxidation.

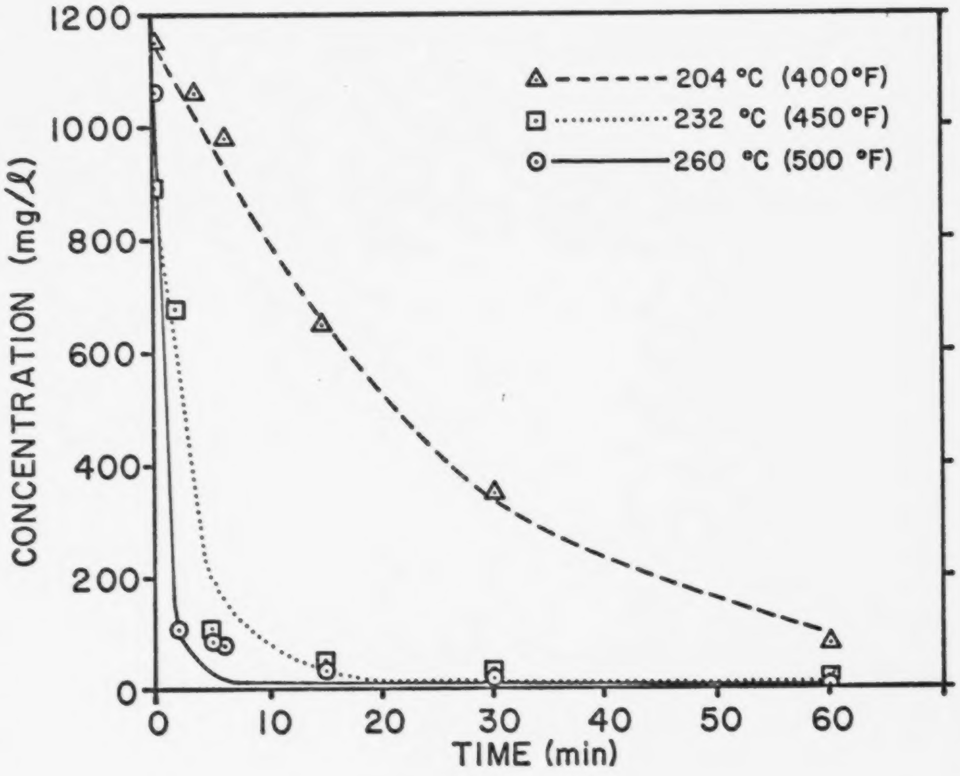


Figure 18. Influence of Temperature on 4-Nitrophenol Destruction During Wet Oxidation.

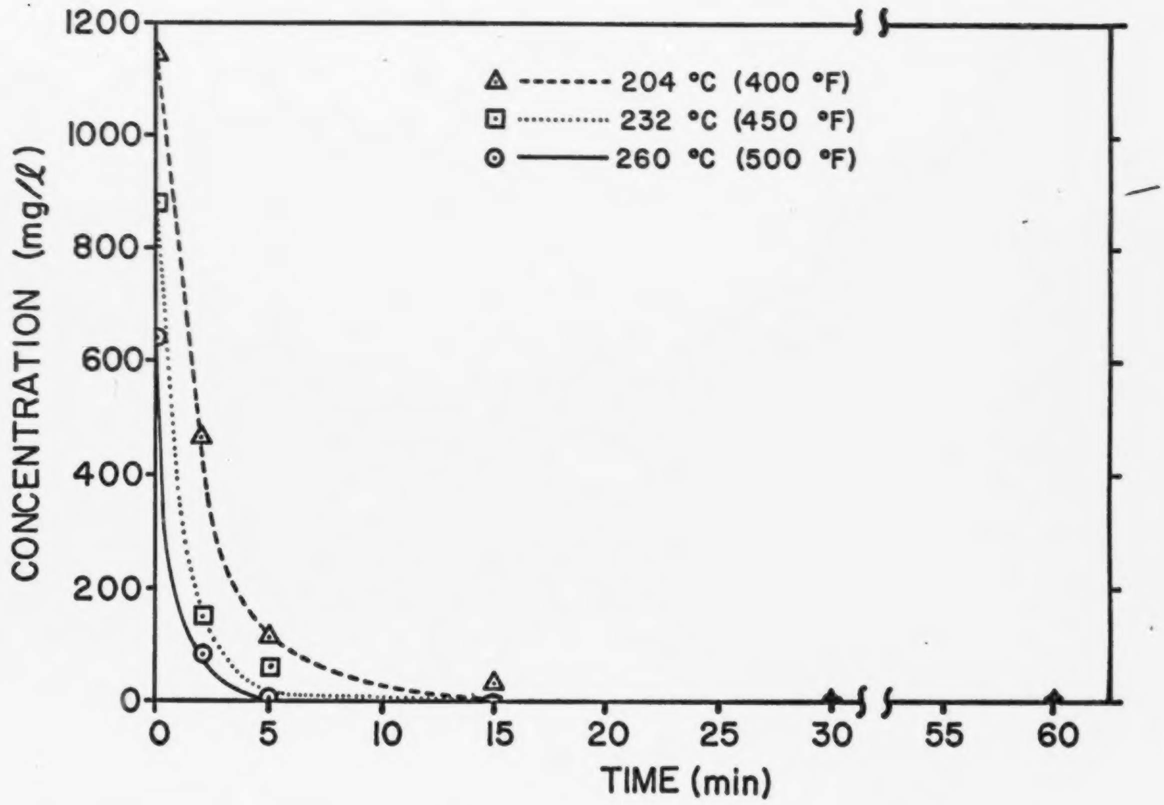


Figure 19. Influence of Temperature on Dimethylphthalate Destruction During Wet Oxidation.

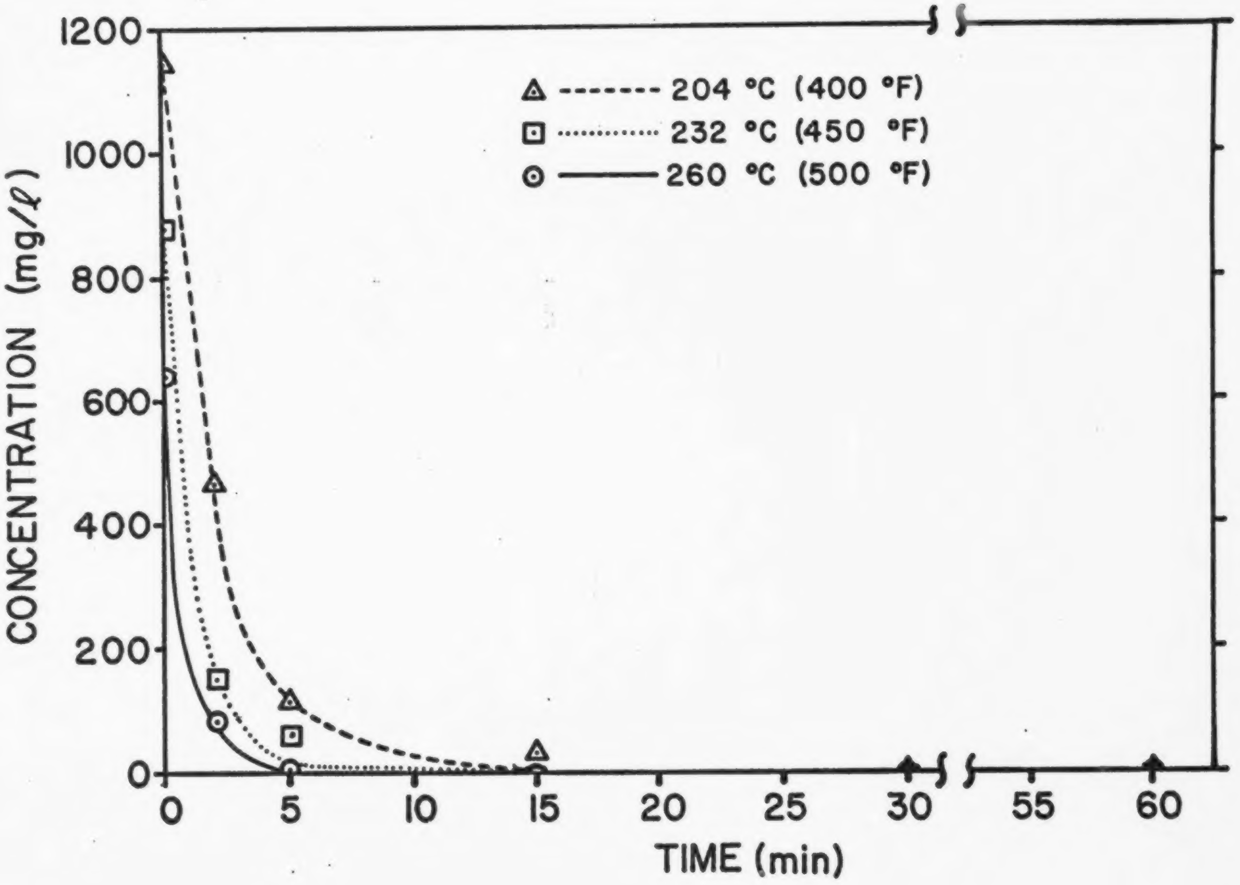


Figure 20. Influence of Temperature on 1,2-Dichloroethane Destruction During Wet Oxidation.

TABLE 13. FIRST ORDER MODEL REMOVAL PARAMETERS, m_1, AND STANDARD ERROR VALUES, s, FOR WET OXIDATION OF SPECIFIC SUBSTANCES

	204°C		232°C		260°C	
	m_1 (min^{-1})	s (min^{-1})	m_1 (min^{-1})	s (min^{-1})	m_1 (min^{-1})	s (min^{-1})
Phenol	0.25	0.02	0.43	0.03	0.59	0.02
2-Chlorophenol	0.04	0.004	0.12	0.02	0.45	0.05
4-Nitrophenol*	0.04	0.003	0.27	0.05	0.94	0.16
1,2-Dimethylphthalate	0.008	0.002	0.036	0.005	0.100	0.008
1,2-Dichloroethane	0.45	0.02	0.84	0.08	1.02	0.004

*Initial concentration is 1000 mg/ℓ, all others are 5000 mg/ℓ.

TABLE 14. PHASIC MODEL REMOVAL PARAMETERS, m_f, FOR INITIAL FAST REACTION FOR WET OXIDATION OF SPECIFIC SUBSTANCES

	204°C	232°C	260°C
	m_f (min^{-1})	m_f (min^{-1})	m_f (min^{-1})
Phenol	0.26	0.42	0.59
2-Chlorophenol	0.06	0.15	0.45
4-Nitrophenol*	0.04	0.28	0.92
1,2-Dimethylphthalate	0.04	0.09	0.12
1,2-Dichloroethane	0.45	0.84	1.02

*Initial concentration is 1000 mg/ℓ, all others are 5000 mg/ℓ.

1. the change in oxygen pressure during the experiment
2. possible volatilization of reactant into the headspace
3. dissolved oxygen concentration as influenced by the overall volumetric mass transfer coefficient

Initial oxygen pressures were on the order of 2 to 2.5 MPa (288 to 360 psig) and decreased to 1 to 1.5 MPa (144 to 216 psig) during the course of reaction as liquid samples were withdrawn and oxygen was utilized. This variation in pressure apparently had little effect on the reaction rate because, as indicated above, removal parameters estimated using only the phasic model based on the first 3 data points were nearly equal to those based on the first order model.

The influence of volatilization can be significant if a large fraction of the reactant resides in the reactor headspace. This can be analyzed by a reactant material balance based on equilibrium between the liquid and vapor phases:

$$-rV_L = V_L \frac{dC}{dt} + V_G \frac{dC_g}{dt} \qquad 25$$

where: V_G = volume of gas in the reactor headspace, L^3

The measured reactant profile reflects C as a fraction of time and can be described by $dC/dt = -m_1 C$.

Assuming that the reactant in the vapor phase is in equilibrium with the liquid gives:

$$\frac{dC_g}{dt} = \frac{d(HC)}{dt} = H \frac{dC}{dt} = -Hm_1 C \qquad 26$$

so that Equation 25 can be written as:

$$r = m_1 \left[1 + \frac{V_G}{V_L} H \right] C \qquad 27$$

Comparison with the second order rate expression (Equation 3) shows that:

$$k_w O_2 = m_1 \left[1 + \frac{V_G}{V_L} H \right] \qquad 28$$

Provided that reasonable values of Henry's constant, H, can be estimated at elevated temperatures, Equation 28 allows the product k_wO_2 to be determined from the measured value of r. It has been shown (43) that H can be related to the vapor pressure and aqueous solubility of a pure substance. Assuming that the solubility, C_a^*, is constant with increasing temperature facilitates rough estimates of H at elevated temperatures by:

$$\frac{H_1}{H_2} = \frac{(P_{v1})\ (T_2)\ (C_{a2}^*)}{(P_{v2})\ (T_1)\ (C_{a1}^*)} \qquad 29$$

where P_{v1} and P_{v2} are vapor pressures of pure substance at temperatures T_1 and T_2, respectively. Using this approach gives rough H values at 0.057 mol/mol and 5.8 mol/mol for phenol and 1,2-dichloroethane, respectively at 204°C. Evaluation of Equation 28 for these substances at 204°C shows that the volatilization is insignificant for phenol as $k_wO_2 = 1.04m_1$, but extremely significant for 1,2-dichloroethane as $k_wO_2 = 5.67m_1$.

Pruden and Le (16) estimated $k_w = 3146$ ℓ/hr·mol for phenol at 200°C. The initial dissolved oxygen in the wet oxidation reactor can be estimated based on this rate constant as:

$$O_2 = \frac{1.04m_1}{k_w} = \frac{1.04\ (0.25\ \text{min}^{-1})\ (60\ \text{min/hr})}{3146\ \ell/\text{hr}\cdot\text{mol}} = 4.96 \times 10^{-3}\ \text{mol}/\ell$$

which is 13% of the saturation value (44). This indicates that under these experimental conditions, reaction in the diffusive film would not be significant.

Variation of the reaction rate constants with temperature can be described by the Arrhenius relationship:

$$k_w = A_f\ \exp\ (-E_a/RT_{abs}) \qquad 30$$

where: A_f = frequency factor, $L^3\ \text{mol}^{-1}\ t^{-1}$

E_a = energy of activation, cal mol^{-1}

R = ideal gas constant, L^3 atm $\text{mol}^{-1}\ T^{-1}$

T_{abs} = absolute temperature, T

Multiplying both sides by O_2 and taking the natural log gives:

$$\ln\ (k_wO_2) = \ln\ (A_fO_2) - (E_a/RT_{abs}) \qquad 31$$

For non-volatile substances, where values of Henry's constant are small ($H < 0.1$ at reactor temperature), Equation 28 indicates that,

$$k_w O_2 \approx m_1 \qquad 32$$

so that, for these substances, the Arrhenius equation can be written as:

$$\ln m_1 = \ln (A_f O_2) - (E_a/RT_{abs}) \qquad 33$$

A plot of the $\ln m_1$ or $\ln m_f$ versus $1/T_{abs}$ should therefore give a straight line with the intercept at $\ln (A_f O_2)$ and a slope of $-E_a/R$. Figure 21 shows such Arrhenius plots based on the removal parameters, m_f, estimated for the phasic model initial fast reaction. Table 15 lists values of the activation energies derived from the slopes of these plots. Table 16 lists activation energy values reported in the literature for wet oxidation of various substances. The range of E_a values found in this study are generally comparable to the range of values reported by others.

Figures 22 and 23 show the influence of temperature on the removal patterns of TOC and COD during wet oxidation of 2-chlorophenol. The curves drawn in these figures represent the modified first order model fit to the data points by nonlinear regression. Table 17 shows the parameter estimates for this model fit to the TOC removal data during wet oxidation of phenol, 2-chlorophenol and 4-nitrophenol. In general, this model fits the data adequately; however, the empirical nature of the model is pointed out by the negative value estimated for C^* for 4-nitrophenol at 204°C. The TOC and COD data both indicated that complete oxidation was not obtainable as a residual concentration of species resistant to wet oxidation remained at the conclusion of the reaction period.

TABLE 17. MODIFIED FIRST ORDER REMOVAL PARAMETERS, m_2 AND C^*, FOR TOC REMOVAL PATTERNS DURING WET OXIDATION

	204°C		232°C		260°C	
	m_2 (min^{-1})	C^* (mg/ℓ)	m_2 (min^{-1})	C^* (mg/ℓ)	m_2 (min^{-1})	C^* (mg/ℓ)
Phenol	0.09	530	0.20	470	0.26	430
2-Chlorophenol	0.05	1190	0.14	860	0.34	540
4-Nitrophenol	0.01	-140	0.22	100	0.73	100

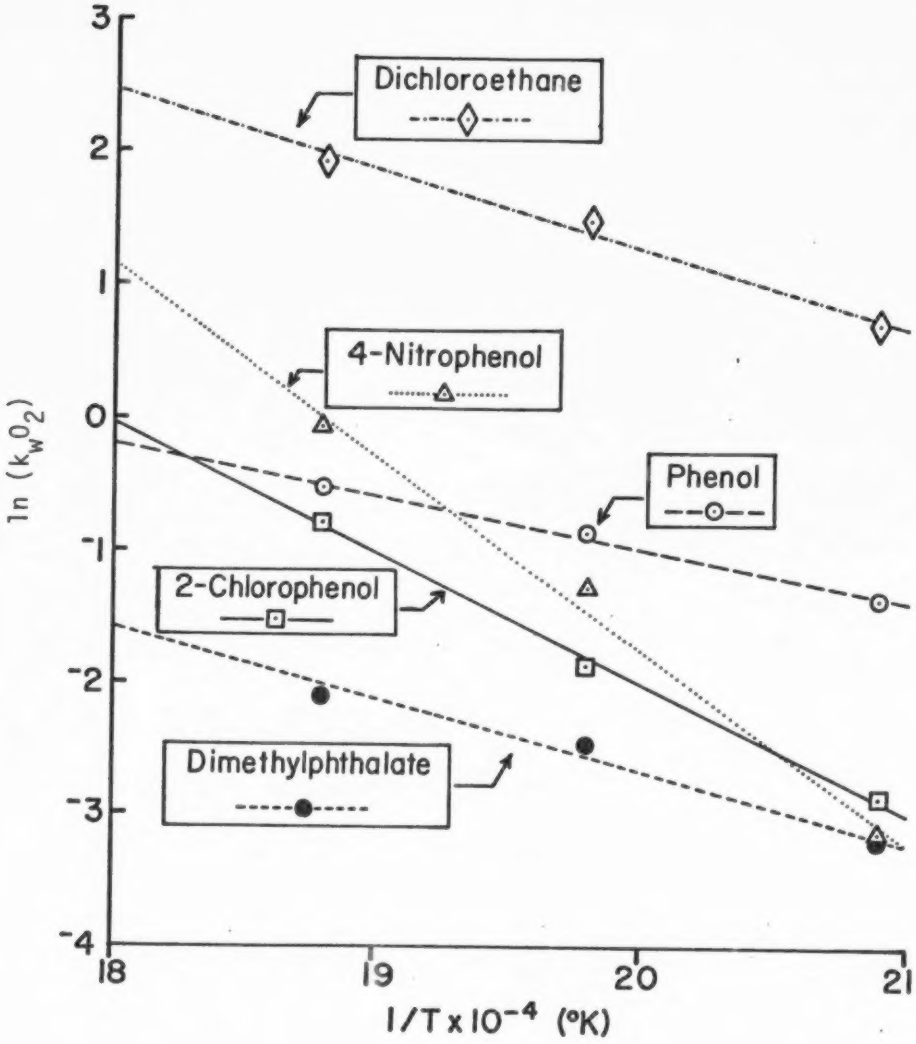


Figure 21. Arrhenius Plots Based on Phasic Model, Initial Fast Reaction.

TABLE 15. SUMMARY OF ACTIVATION ENERGY VALUES BASED ON PHASIC MODEL, INITIAL FAST FIRST ORDER REACTION

Substance	E_a (Kcal/mol)
Phenol	7.9
2-Chlorophenol	19.3
4-Nitrophenol*	28.8
1,2-Dimethylphthalate	23.9
1,2-Dichloroethane	11.6

*Initial concentration was 1000 mg/ℓ, all others were at an initial concentration of 5000 mg/ℓ.

TABLE 16. LITERATURE VALUES OF ACTIVATION ENERGIES FOR WET OXIDATION

Substance	Source	E_a (Kcal/mol)
Propionic acid	Day *et al*. (22)	33.0
Phenol	Pruden and Le (16)	10.8
Nitrilotriacetic acid	Pruden and Le (16)	13.0
Glucose	Ploos Van Amstel (18)	23
Glucose	Skaates *et al*. (19)	15.4
Phenol	Sadana and Katzer (56) (catalytic reaction)	24 to 48 (depending on size of catalyst particle)

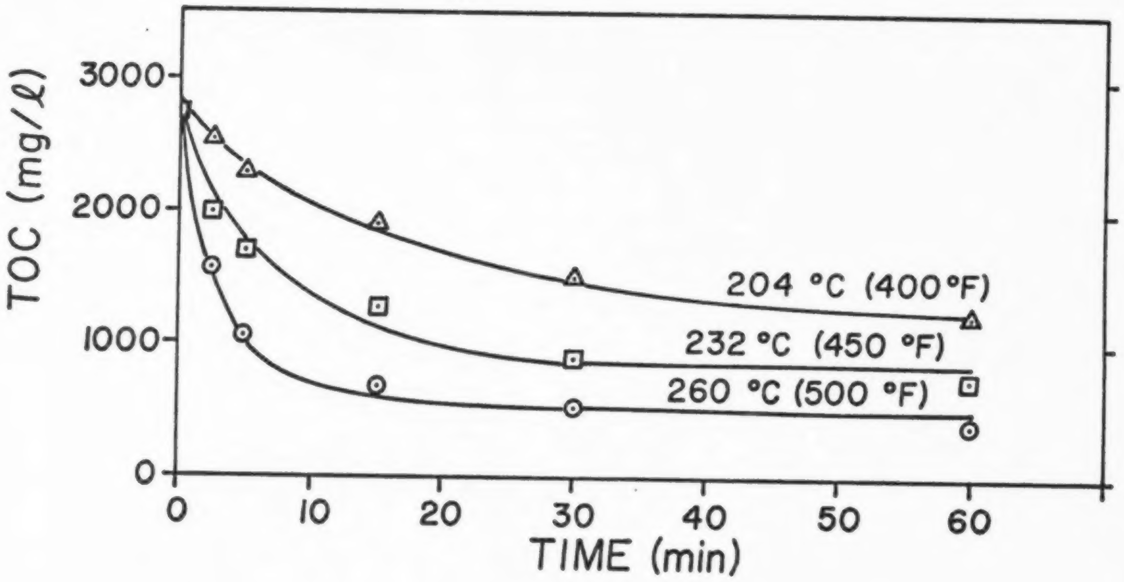


Figure 22. Influence of Temperature on TOC During Wet Oxidation of 2-Chlorophenol.

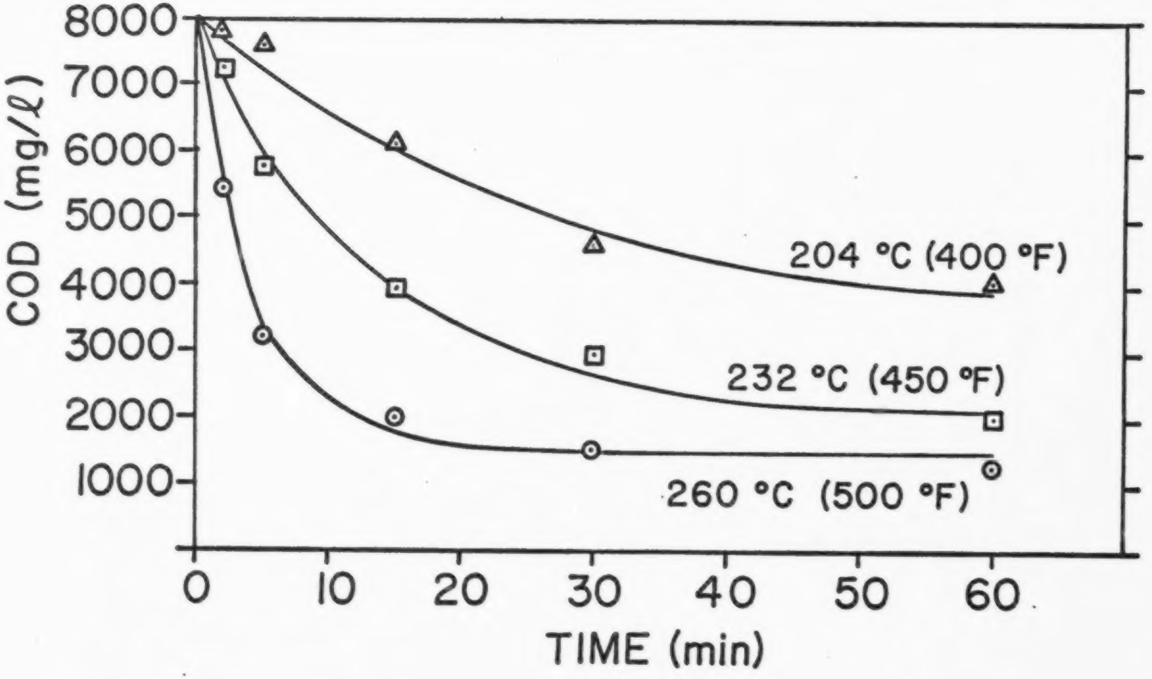


Figure 23. Influence of Temperature on COD Destruction During Wet Oxidation of 2-Chlorophenol.

Influence of Initial pH on Removal Patterns

Figures 24 to 26 illustrate the influence of initial pH on the removal patterns of specific substance, TOC and COD during wet oxidation of 2-chlorophenol. Figure 27 shows this influence on chloride generation. Although the alkaline pH markedly increased the rate of specific substance disappearance and chloride generation, it increased the initial rate of TOC and COD disappearance only slightly. Moreover, the higher initial pH values produced larger residual concentrations of TOC and COD at the conclusion of the reaction period. Table 18 summarizes the influence of initial pH on the parameter estimates for the first order model fitted to the specific substance removal data and the modified first order model fitted to the TOC removal data.

TABLE 18. INFLUENCE OF INITIAL pH ON WET OXIDATION REMOVAL PARAMETER ESTIMATES, m_1, m_2 and C^*

		Control pH = 4.5			Alkaline pH = 9.5		
		Substance	TOC		Substance	TOC	
		m_1 (min^{-1})	m_2 (min^{-1})	C^* (mg/ℓ)	m_1 (min^{-1})	m_2 (min^{-1})	C^* (mg/ℓ)
Phenol	232°C	0.43	0.20	470	0.54	0.24	1440
2-Chlorophenol	204°C	0.04	0.05	1190	0.38	0.07	1300
2-Chlorophenol	232°C	0.12	0.14	860	0.62	0.19	1450
1,2-Dichloroethane	232°C	0.85	-	-	1.15	-	-

Influence of Copper Catalyst on Removal Patterns

Figures 28 and 29 show the influence of cupric ion on the removal patterns of specific substance and TOC during wet oxidation of 2-chlorophenol at 204°C. A catalytic effect is evident as the copper increased both the rate and extent of removal in both cases. Figure 30 shows the influence of 50 mg/ℓ and 500 mg/ℓ copper catalyst on the removal of 1,2-dimethylphthalate. Removals increased substantially with increasing catalyst concentration. Figure 31 shows that without copper catalyst, wet oxidation was ineffective in reducing the COD of 1,2-dimethylphthalate. Product analysis indicated that, in this case, 1,2-dimethylphthalate was mostly hydrolyzed to methanol and phthalic acid. Figures 32 and 33 show the methanol and phthalic acid profiles with and without copper catalyst.

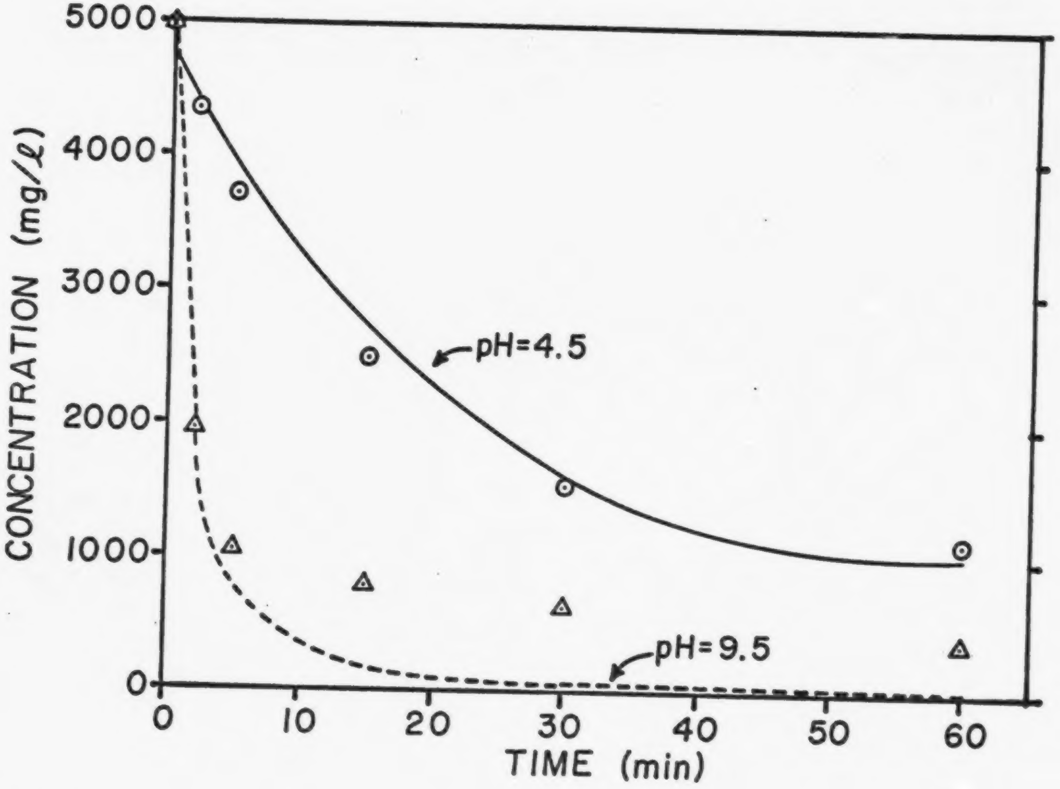


Figure 24. Influence of Initial pH on 2-Chlorophenol Destruction During Wet Oxidation at 232°C.

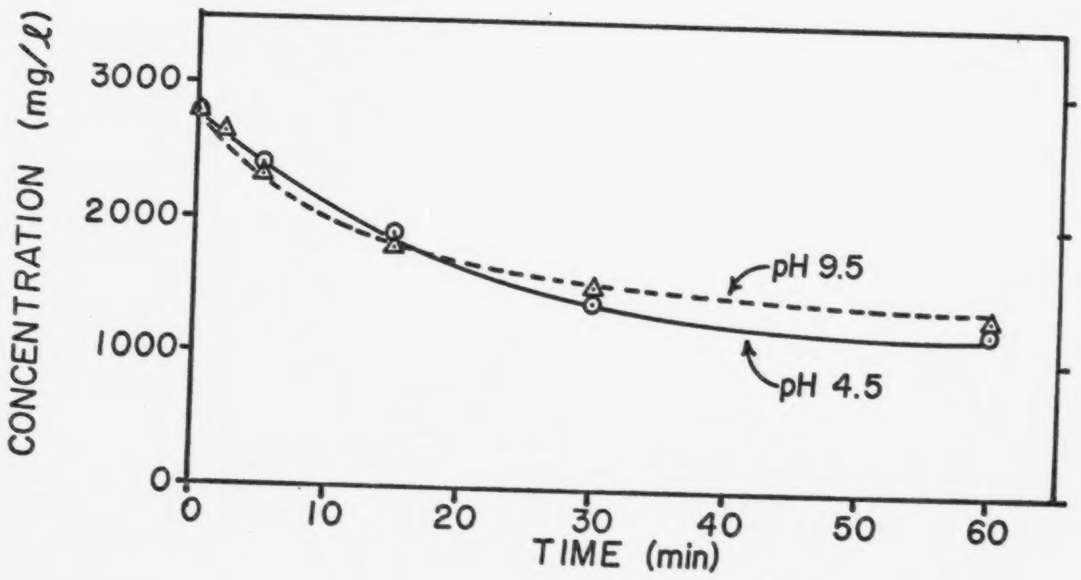


Figure 25. Influence of Initial pH on TOC Destruction During Wet Oxidation of 2-Chlorophenol at 204°C.

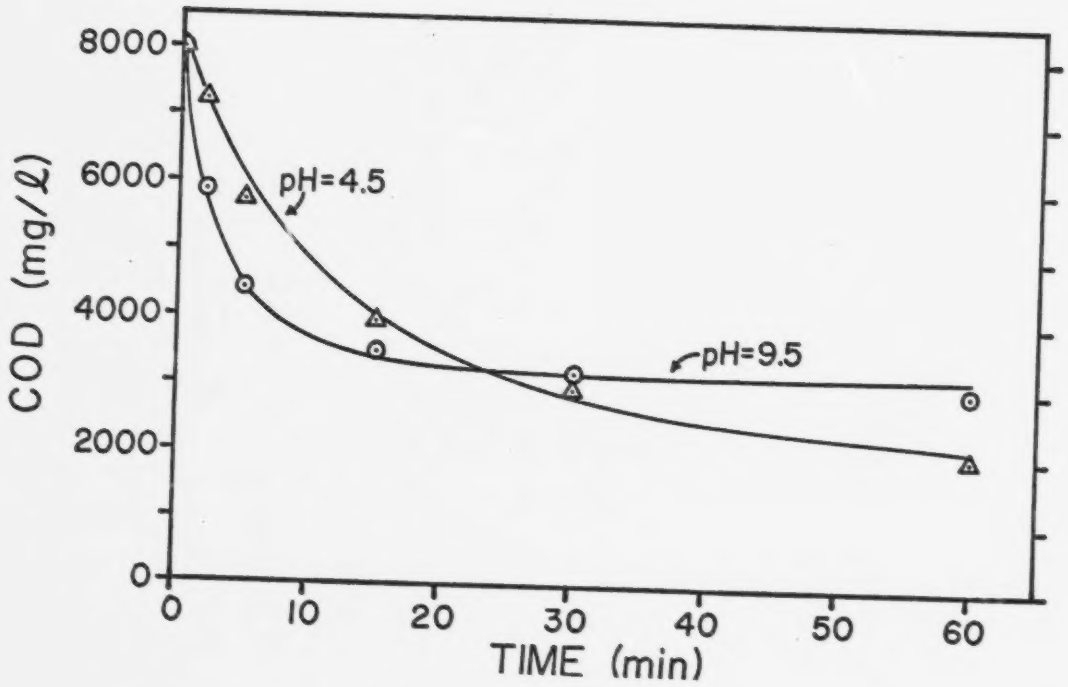


Figure 26. Influence of Initial pH on COD Destruction During Wet Oxidation of 2-Chlorophenol at 232°C.

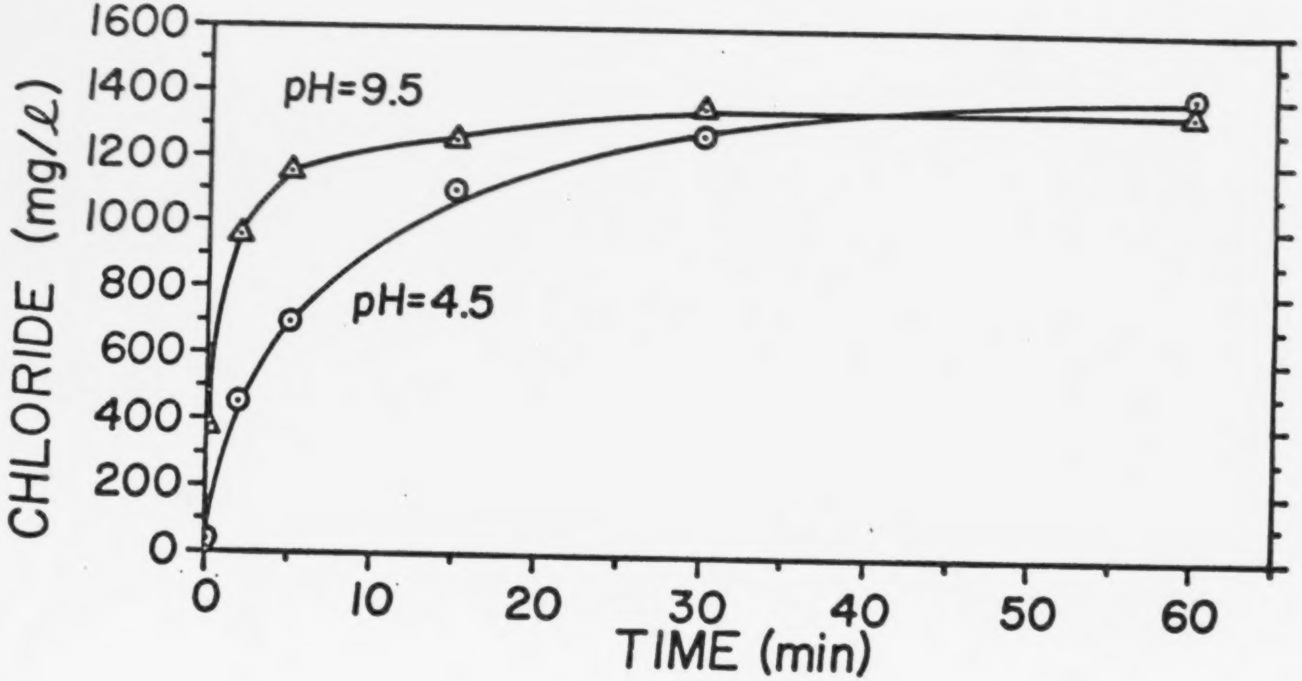


Figure 27. Influence of Initial pH on Chloride Generation During Wet Oxidation of 2-Chlorophenol at 232°C.

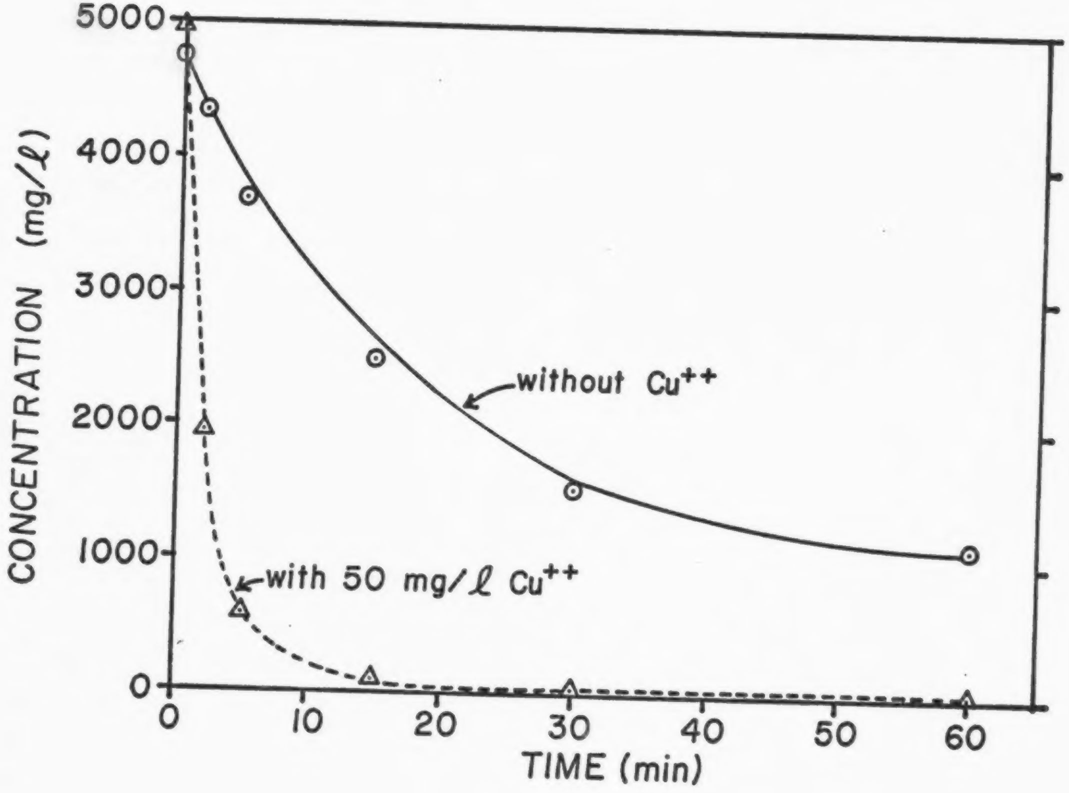


Figure 28. Influence of Copper Catalyst on 2-Chlorophenol Destruction During Wet Oxidation at 204°C.

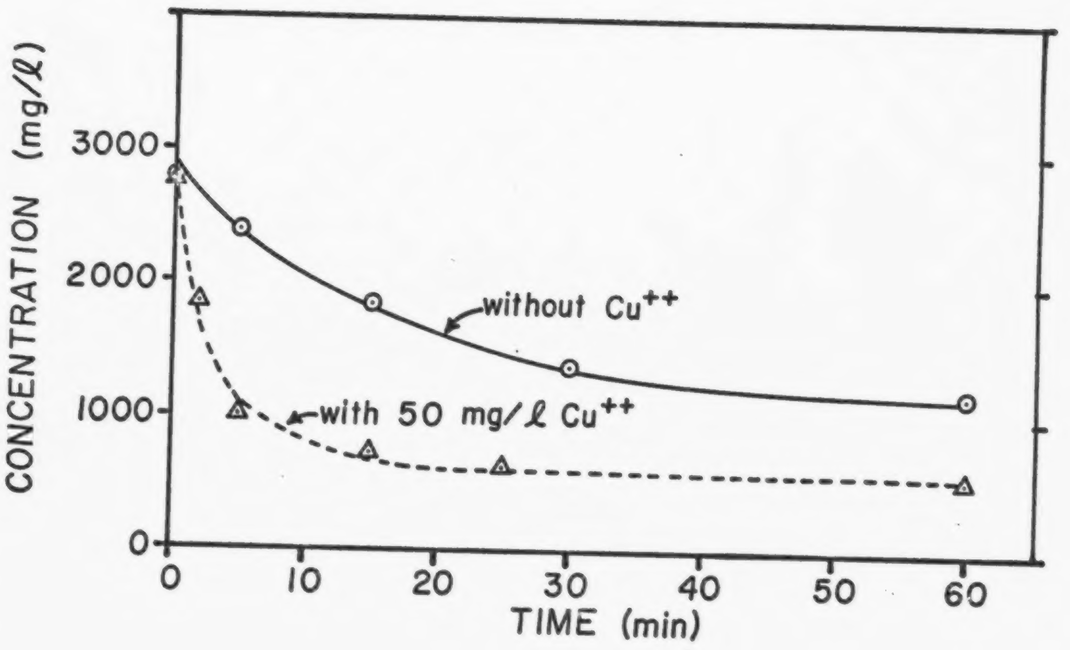


Figure 29. Influence of Copper Catalyst on TOC Destruction During Wet Oxidation of 2-Chlorophenol at 204°C.

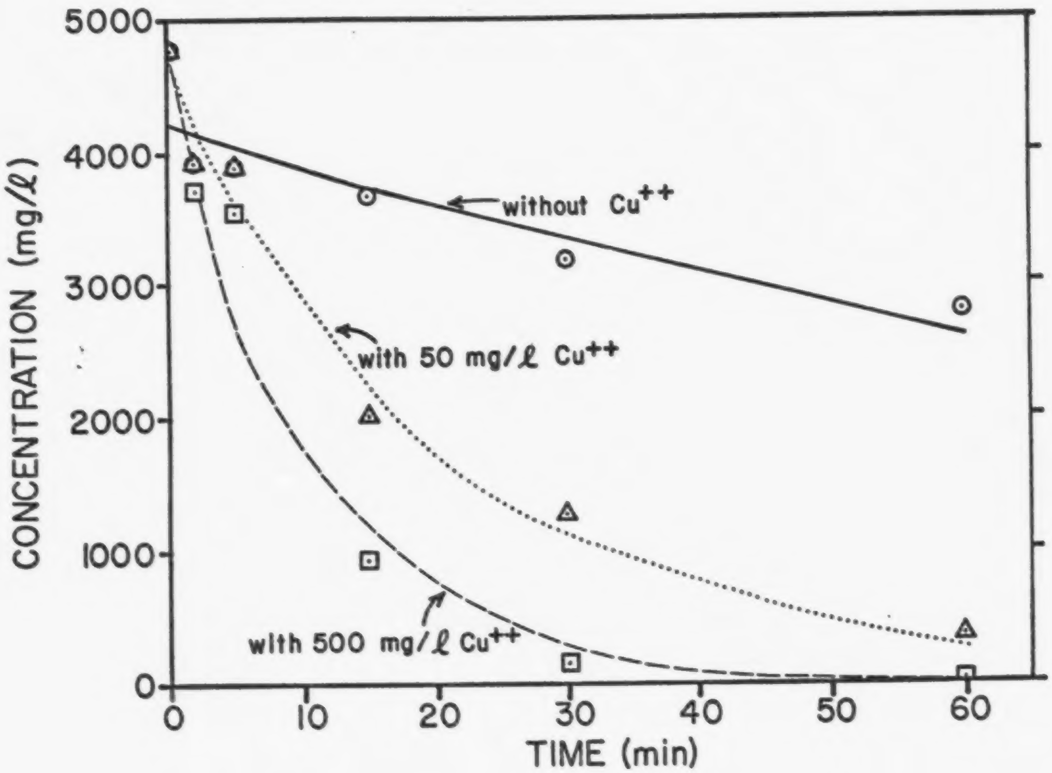


Figure 30. Influence of Copper Catalyst on Dimethylphthalate Destruction During Wet Oxidation at 204°C.

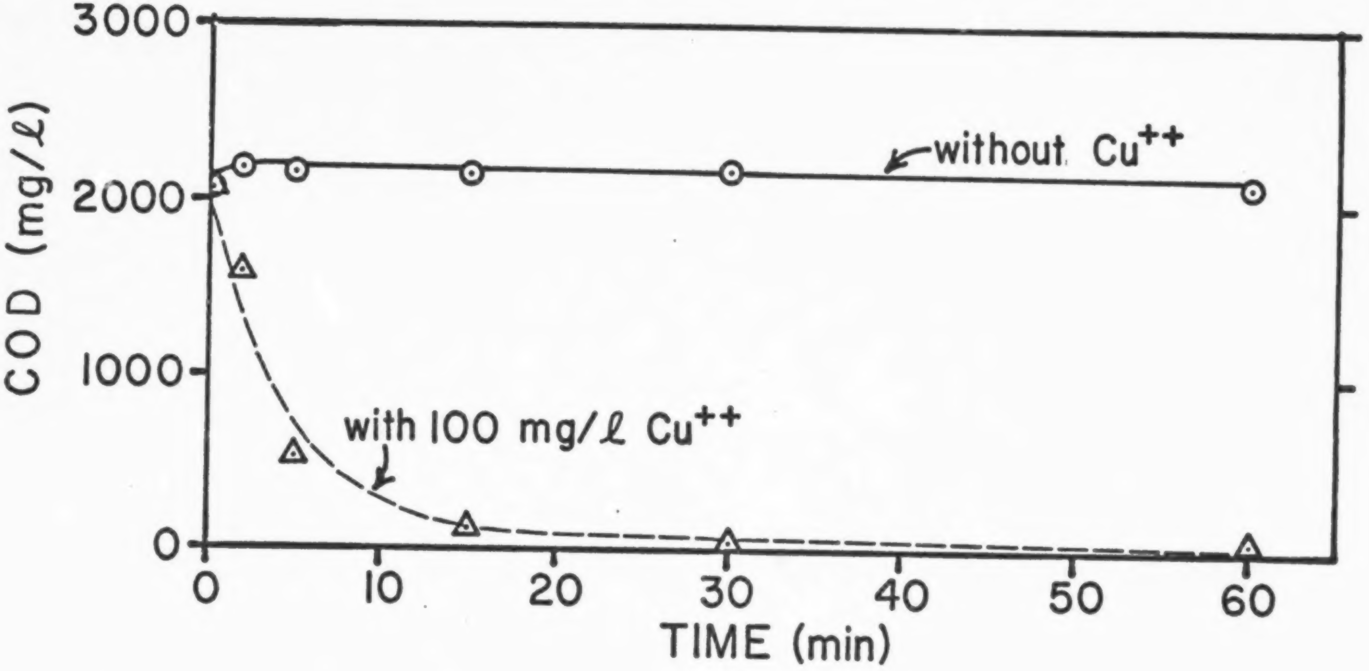


Figure 31. Influence of Copper Catalyst on COD Destruction During Wet Oxidation of Dimethylphthalate at 260°C.

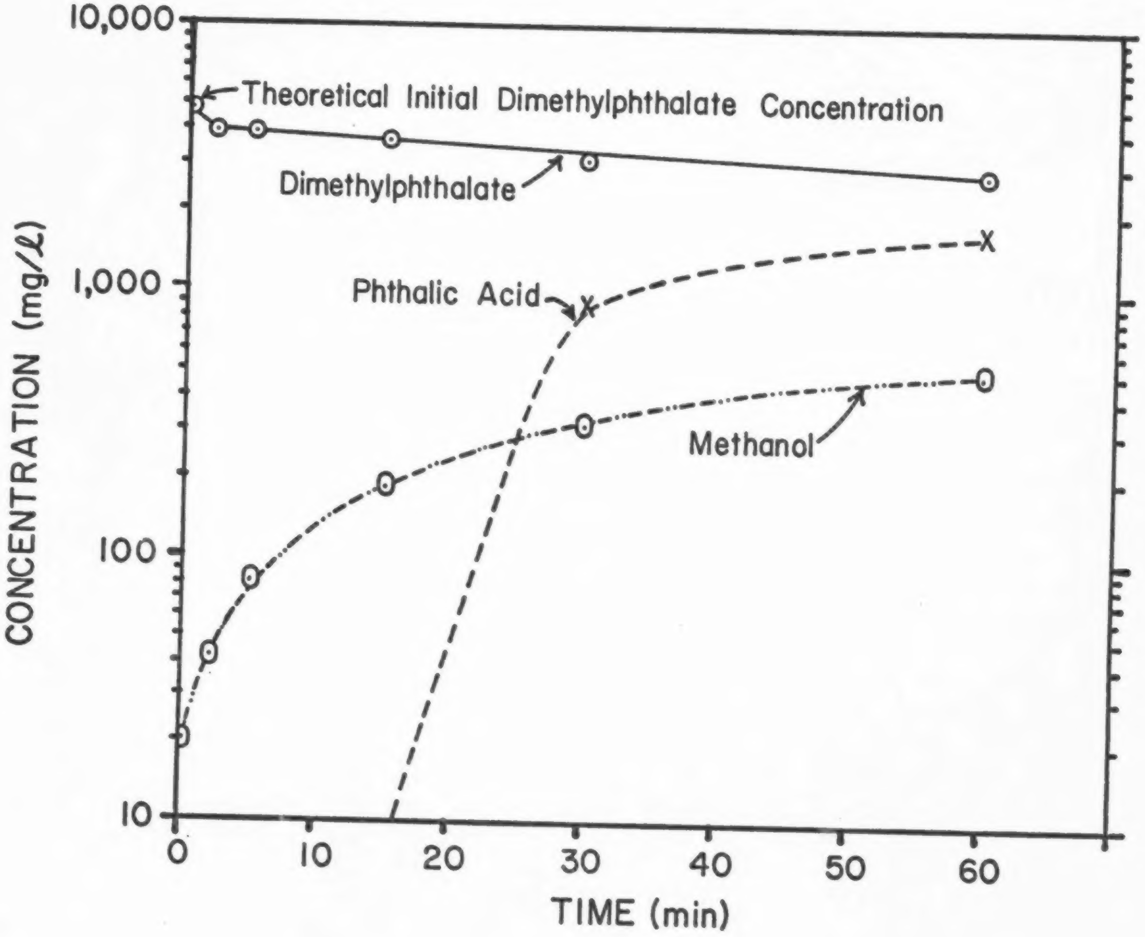


Figure 32. Organic Carbon Transformations During Wet Oxidation of Dimethylphthalate at 204°C.

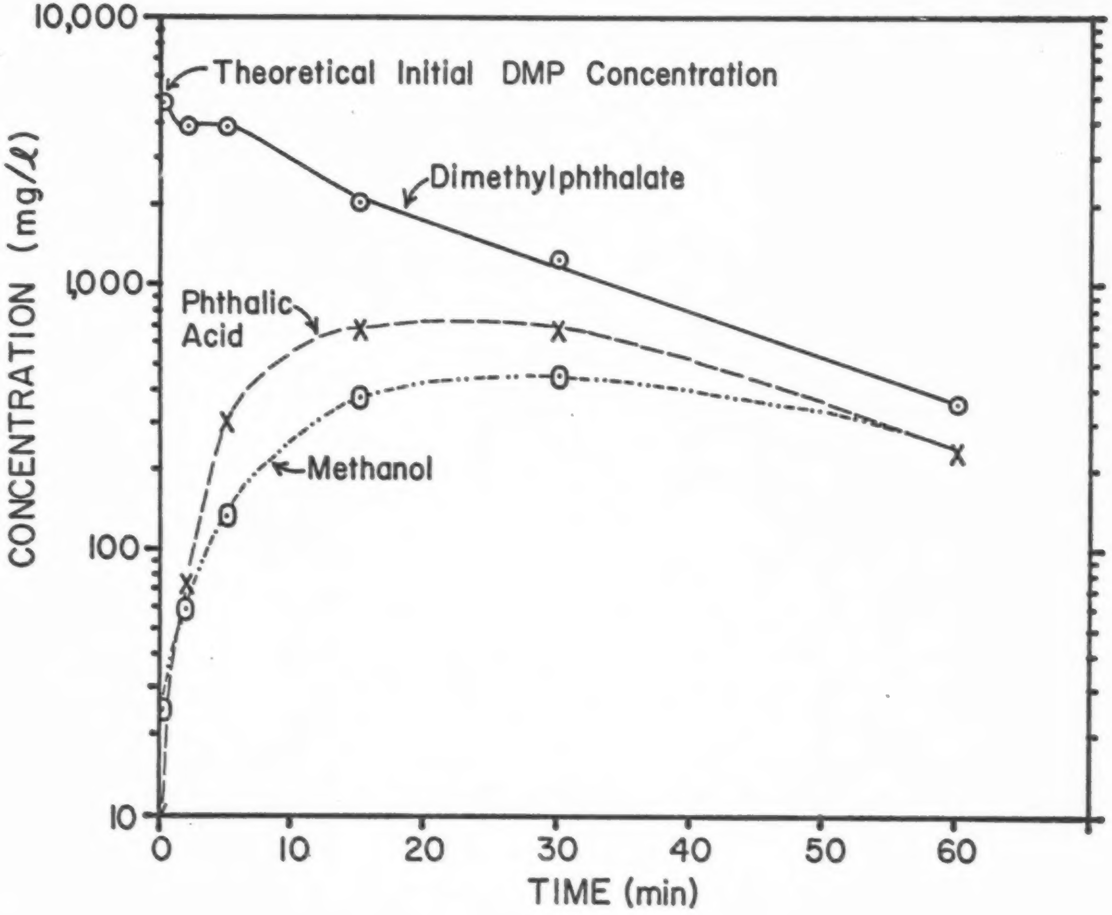


Figure 33. Organic Carbon Transformations During Wet Oxidation of Dimethylphthalate at 204°C with 50 mg/ℓ Copper Catalyst.

Cupric ion also increased the rate and extent of wet oxidation of phenol and 4-nitrophenol. Table 19 summarizes the removal parameters estimated for specific substance and TOC by the various models. In almost all cases, cupric ion increased the removal parameters. For TOC, copper catalyst decreased the estimates of C^* given by the modified first order model.

The effect of catalysts in wet oxidation has been studied by others. Brett and Gurnham (17) investigated the effect of hydrogen peroxide and various metal salts on wet oxidation. Miller *et al.* (45) described a bromide nitrate cocatalyst system that was reported to achieve high organic destruction rates at much lower temperatures than conventional wet oxidation. Chowdhury and Ross (21) in an investigation of several catalysts and their effect on the wet oxidation of a strong wastewater found that the ferric ion, the cupric ion, along with hydrogen peroxide were effective catalysts over a wide pH range.

The use of the catalyst clearly increases the rate and extent of oxidation. It would be an effective means of obtaining high removals at shorter reaction times and at less severe operating conditions, which would lead to lower capital costs. However, many catalysts are toxic themselves and would have to be removed from the effluent stream. Zimpro Inc., has developed a sulfide precipitation process for removing copper catalyst from wet oxidation effluents (46).

ORGANIC CARBON TRANSFORMATIONS DURING WET OXIDATION

Specific Organic Substances

Figures 34 and 35 show profiles of organic carbon transformations measured during wet oxidation of phenol and 2-chlorophenol at 232°C. These data indicate that formic and acetic acid were the two principal organic compounds produced. Succinic acid, acetaldehyde and acetone were present along with lesser amounts of oxalic and muconic acids. The substances detected during wet oxidation of phenol, 2-chlorophenol and 4-nitrophenol were similar. However, phenol and its oxidation products generally reacted more quickly than either of the substituted phenols.

Wet oxidation of 1,2-dimethylphthalate produced phthalic acid, methanol and smaller amounts of formic, acetic and maleic acids. The major reactant products detected during wet oxidation of 1,2-dichloroethane were propionic and acetic acids. Smaller amounts of acetaldehyde, methanol and acetone were also detected. These samples were only analyzed by direct aqueous injection; therefore, formic, muconic, maleic, succinic and oxalic acids would not have been detected.

TABLE 19. INFLUENCE OF COPPER CATALYST ON KINETIC REMOVAL PARAMETERS

		Specific Substance		Total Organic Carbon					
		First Order		Phasic		Modified First Order			
		Control	Copper Catalyst	Control	Copper Catalyst	Control		Copper Catalyst	
Substance	Temperature (^oC)	m_1 (min^{-1})	m_1 (min^{-1})	m_f (min^{-1})	m_f (min^{-1})	m_2 (min^{-1})	C^* (mg/ℓ)	m_2 (min^{-1})	C^* (mg/ℓ)
Phenol	204	-	-	-	-	0.09	530	0.11	160
Phenol	232	0.43	2.33	0.17	0.56	0.20	470	0.64	180
Phenol	260	-	-	-	-	0.26	430	0.57	110
2-Chlorophenol	204	0.04	0.45	-	-	0.05	1190	0.31	630
2-Chlorophenol	232	0.12	0.73	-	-	0.14	860	0.67	360
4-Nitrophenol	204	0.04	0.21	0.07	0.15	0.12	390	0.11	105
4-Nitrophenol	232	0.27	0.29	0.15	0.25	0.34	690	0.26	75
1,2-Dimethylphthalate	204	0.008	0.042	0.06	0.08	0.01	2200	0.01	-900
1,2-Dimethylphthalate	260	0.100	0.32	-	0.19	-	-	0.20	17

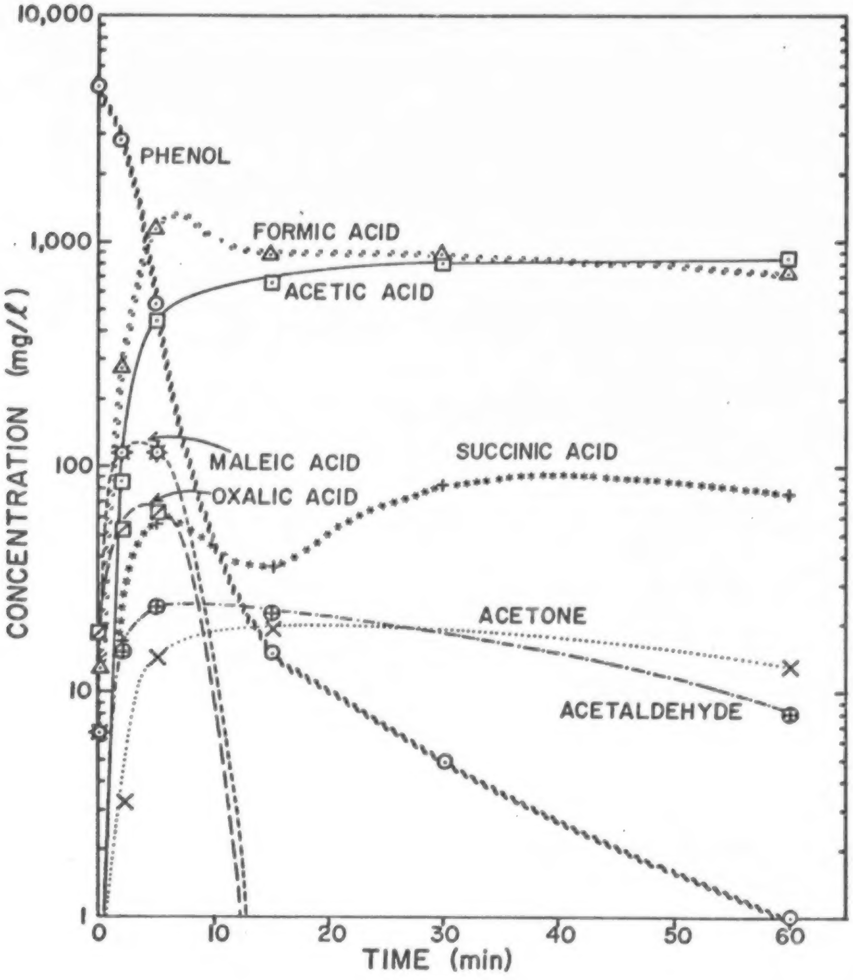


Figure 34. Organic Carbon Transformations During Wet Oxidation of Phenol at 232°C.

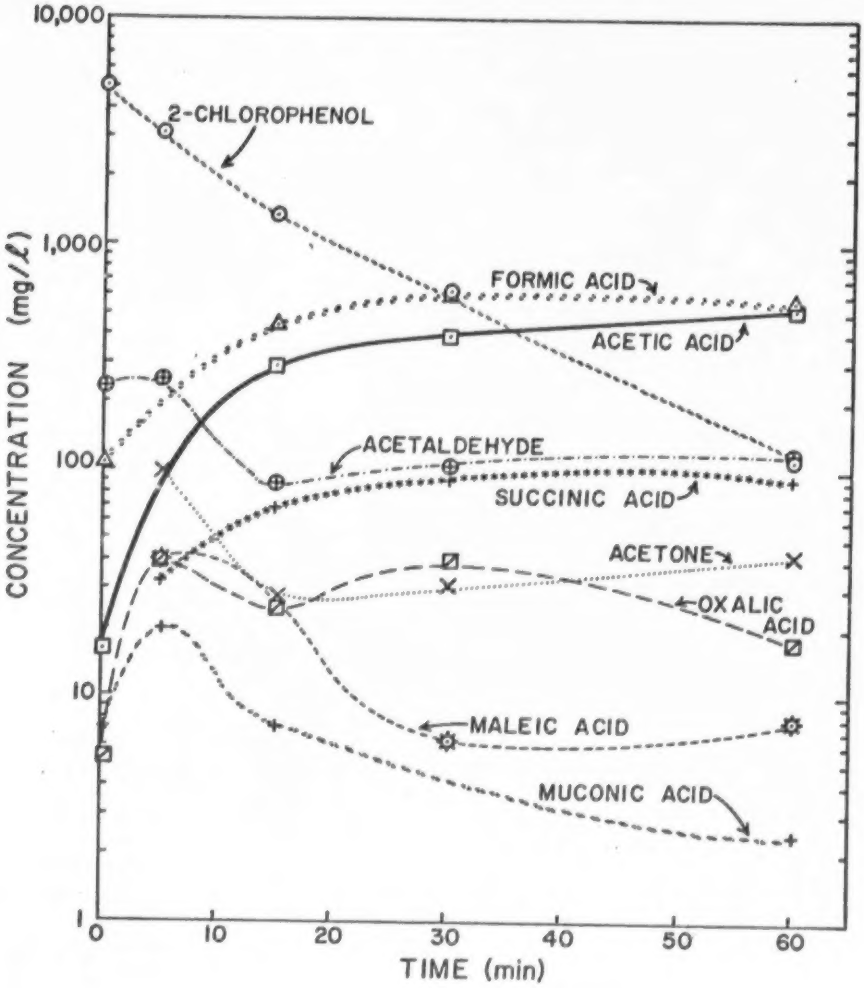


Figure 35. Organic Carbon Transformations During Wet Oxidation of 2-Chlorophenol at 232°C.

The product data for each substance indicated that the type of final products and intermediates formed did not differ from run to run. The concentrations of each varied with the type of treatment as well as with temperature. Generally, as the severity of treatment increased, more of the organic products were converted to carbon dioxide.

It should be noted that the individual compounds measured by GC analysis failed to account for a significant fraction of the measured TOC. The smallest fraction accounted for within a given experiment usually occurred at the 5 and 15 minute samples which were taken during a period of high intermediate product generation. These results were probably caused by production of intermediate products not detectable by the GC methods employed. The fraction of organic carbon accounted for at the conclusion of the reaction period varied between experiments and typically ranged from 40 to 95% with the lowest values observed in experiments in which copper catalyst was employed. This unidentified organic fraction makes it difficult to hypothesize or explain mechanisms for reactions occurring during wet oxidation.

It is interesting to interpret the TOC removal kinetics in light of the product analysis profiles. The phasic fast model represented the first 15 minutes of reaction which was the time period of greatest substance destruction. The slow phase represented the remaining reaction period during which the rate of reaction slowed significantly because the intermediate substances were oxidized more slowly. This explains why the TOC profiles were described by the modified first order and phasic models but not by conventional first order kinetics applied over the entire reaction period.

Comparison of the wet oxidation organic carbon transformations (Figures 34 and 35) with the ozonation organic acid profiles (Figures 14 and 15) indicates that acetic acid was not evident during ozonation, although it was a major end product of wet oxidation. Conversely, oxalic acid was a relatively minor product during wet oxidation, but was an important product of ozonation.

The carbon transformation results observed during wet oxidation are in general agreement with results reported by others. Day *et al.* (22) studied wet oxidation of propionic acid and reported that 44% of the initial carbon was converted to acetaldehyde and acetic acid. Teletzke *et al.* (15) reported the production of fatty acids, amino acids and simple sugars during the wet oxidation of sewage sludge. Fassell (9) in a study of the wet oxidation of sludge found that the liquid effluent consisted primarily of acetic acid, with lesser amounts of propionic acid, formic acid, and acetone present.

Basically, the wet oxidation process has been found to convert large molecules to carbon dioxide, water and simpler more oxygenated organic compounds. These organics consist mainly of low molecular weight carboxylic acids which are resistant to any further wet oxidation treatment, but are generally biodegradable.

Petrochemical Waste

A sample of a petrochemical waste was obtained from an operating facility for which wet oxidation appeared to be a feasible treatment alternative. The sample was taken from a particularly strong process waste stream (COD = 250,000 mg/ℓ) and could be diluted through the addition of other, less strong, waste streams. Section 7 of this report discusses the preliminary design and economics of a wet oxidation process capable of treating this stream combined with other wastes and diluted to a COD of 70,000 mg/ℓ.

The sample of strong process waste was diluted with distilled water (by a factor of 20) and subjected to batch wet oxidation at an initial pH of 6.9 and temperature of 260°C. The results are given below and showed a rapid initial decrease followed by a slower decrease in COD.

time (min)	0	5	30	60
% COD reduction	0	50%	54%	60%

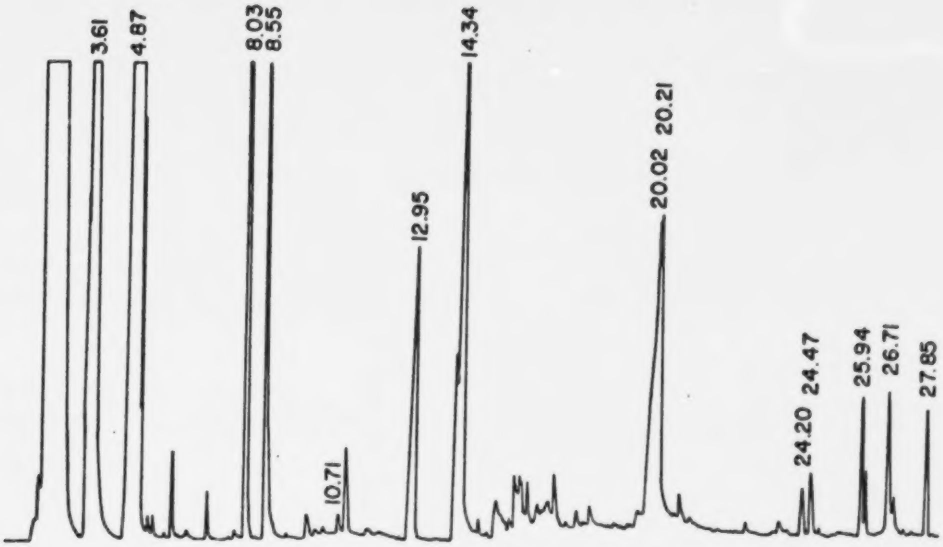
Table 20 compares the characteristics of the waste before and after wet oxidation.

TABLE 20. CHARACTERISTICS OF PETROCHEMICAL WASTE BEFORE AND AFTER WET OXIDATION

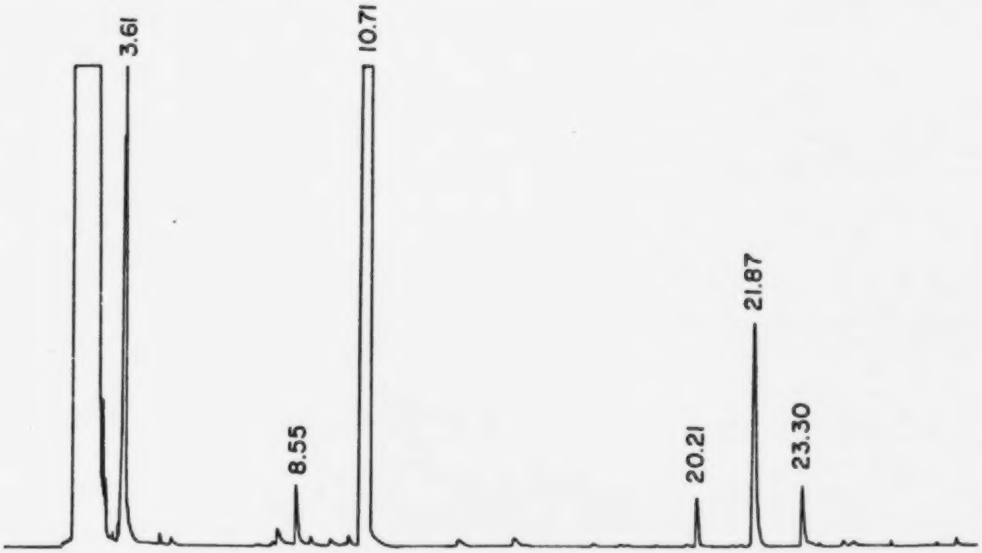
	Raw Waste	After 1 hour Wet Oxidation at 260°C
COD (mg/ℓ)	250,000	100,000
Ultimate BOD (mg/ℓ)	200,000	90,000
BOD_5 (mg/ℓ)	50,000	60,000

Wet oxidation reduced the COD and ultimate BOD by 60 and 55%, respectively. However, the BOD_5 was increased by wet oxidation indicating an improvement in both the rate and extent of biodegradability.

Samples of the raw waste and wet oxidation effluent were subjected to an acid extraction with methylene chloride (100 ml wastewater at pH 2 extracted with 25 ml) and the extract was analyzed by GC using an SP 2100 silica capillary column (temperature programmed, 30°C to 250°C at 25°C/min). Figure 36 shows the chromatograms of the extracts before and after wet oxidation.



Chromatogram of Methylene Chloride Extract of Raw Wastewater.



Chromatogram of Methylene Chloride Extract of Wastewater Following Wet Oxidation.

Figure 36. Comparison of Chromatograms of Petrochemical Waste Extracts Before and After Wet Oxidation.

Comparison of these chromatograms indicates that wet oxidation effectively destroyed many of the peaks shown on the chromatogram of the raw wastewater extract. In addition, a few "product peaks" appear only on the chromatogram of the wastewater following wet oxidation. Attempts were made to identify the peaks through GC-MS but were inconclusive. Table 21 lists the peaks identified by retention times along with the percentage reduction (as measured by area counts) achieved by wet oxidation.

Detoxification by Wet Oxidation

In an effort to assess the overall effectiveness of wet oxidation in mitigating the toxic effects of pollutants, comparative bioassays were conducted on certain substances and wastes before and after wet oxidation. Two types of bioassay were employed:

a) *Salmonella* mutagenicity (Ames) test (47)

b) *Daphnia magna* EC-50 test (48)

The *Salmonella* mutagenicity test uses a specially constructed set of "tester" strains of *S. typhimurium* which are deficient in the ability to synthesize the amino acid, histidine (his$^-$). A mutagen may enter the cell and cause a reverse mutation, restoring the ability of the strain to grow without an external source of histidine. When a test substance is added to viable cells of the his$^-$ mutant, its effectiveness as a mutagen is reflected in the numbers of his$^+$ colonies that arise in the population attempting to grow on histidine-free synthetic agar. This procedure will also indicate general toxicity if the number of mutants/plate with the sample is far less than the number of spontaneous revertants (control plates without the sample). This test was conducted on 4-nitrophenol, 1,2-dimethylphthalate and the petrochemical waste before and after wet oxidation. The mutagenicity test results are presented in detail elsewhere (49) and indicated that:

a) 1,2-Dimethylphthalate and its wet oxidation products were neither toxic nor mutagenic at the concentrations tested.

b) 4-Nitrophenol was neither toxic nor mutagenic at the concentrations tested. However, results of the 4-nitrophenol wet oxidation products suggested the presence of a direct-acting (microsomal metabolic activation not required) frameshift mutagen. By contrast, tests conducted on ozonated solutions of 4-nitrophenol suggested the presence of a direct-acting base-pair mutagen.

TABLE 21. COMPARISON OF ORGANIC CONSTITUENTS IN PETROCHEMICAL WASTEWATER EXTRACT BEFORE AND AFTER WET OXIDATION

Peak Retention Time (Min)	Raw Wastewater (Area Counts)	Wastewater After Wet Oxidation (Area Counts)	% Reduction
3.61	11630	541	95
4.87	9310	-	100
8.03	1709	-	100
8.55	1575	165	90
10.71	-	10920	Product
12.95	1201	-	100
14.34	2325	-	100
20.02	1753	-	100
20.21	-	104	Product
21.87	-	623	Product
23.30	-	165	Product
24.20	111	-	100
24.47	145	-	100
25.94	255	-	100
26.71	325	-	100
27.85	278	-	100

c) The raw petrochemical waste was toxic to the tester strain. Consequently, the mutagenicity of the raw waste could not be assessed. The results of the petrochemical waste wet oxidation products suggested the presence of a direct-acting frame-shift mutagen which may or may not have been present in the raw waste.

The Daphnia bioassay test was conducted on phenol, 2-chlorophenol and 4-nitrophenol before and after wet oxidation. The methods used incorporated pH adjustment and followed those outlined by EPA (48). The results are presented in detail elsewhere (50) and indicated that wet oxidation achieved significant detoxification. This was quantified in terms of the "detoxification factor" which represents the factor by which the test solution (prior to wet oxidation) must be diluted to achieve the same acute toxicity level as measured for the test solution following wet oxidation. For example, a detoxification factor of 40 means that the initial solution of specific substance (usually at a concentration of 5000 mg/ℓ) had to be diluted by a factor of 40 (2.5 ml to 100 ml) to yield a solution equivalent in acute toxicity to the initial solution after one hour of wet oxidation. The percent detoxification for this example would be:

$$100 - \frac{100}{40} = 97.5\%$$

Tables 22 summarizes the detoxification factors and percentages measured for the substances and conditions tested. These results are, in general, comparable to those reported by Randall and Knopp (23).

TABLE 22. RESULTS OF DAPHNIA BIOASSAYS ON SOLUTIONS OF SPECIFIC SUBSTANCES AFTER WET OXIDATION

Specific Substance (48 hour EC-50)	Wet Oxidation Conditions	Detoxification Factor	Percent Detoxification
Phenol (6.6 mg/ℓ)	232°C	36.3	97.2
2-Chlorophenol (3.9 mg/ℓ)	232°C	40.3	97.5
2-Chlorophenol (3.9 mg/ℓ)	232°C Alkaline	120.6	99.2
2-Chlorophenol (3.9 mg/ℓ)	204°C Alkaline	18.7	94.7
4-Nitrophenol (7.7 mg/ℓ)	204°C	9.5	89.5
4-Nitrophenol (7.7 mg/ℓ)	260°C	20	95

SECTION 7

APPLICATION OF WET OXIDATION TO INDUSTRIAL WASTE TREATMENT

The purpose of this section is to illustrate the application of wet oxidation to treatment of a high strength industrial waste. This has been done through the design and economic evaluation of a wet oxidation process to treat a problem wastewater stream produced in an existing petrochemical facility. The petrochemical waste discussed in Section 6 is a major component of this waste stream. The characteristics of the composite waste stream are:

COD	7% or 70,000 mg/ℓ
Temperature	$21^{\circ}C$
pH	highly caustic
Average generation rate	37.85 ℓ/min (10 gal/min)

The waste posed a problem because it inhibited the biological treatment facility at the plant site and was being barrelled and hauled at considerable expense. Wet oxidation appeared to be an attractive alternative because of this biological inhibition and because the relatively high COD of the waste indicated that energy recovery would be feasible. Furthermore, the petrochemical plant could utilize the energy recovered in the form of 50 psia steam. A credit of $13.21 per 1000 Kg of steam ($6 per million BTU) was therefore available.

Batch wet oxidation tests indicated that, at a reactor temperature of $232^{\circ}C$ ($450^{\circ}F$) and excess oxygen pressure, a COD reduction of 73% could be obtained with a residence time of 60 minutes. The subsequent design and economic evaluation was based on this COD reduction, temperature and residence time. Other design data are:

Cooling water temperature	$21^{\circ}C$
Cooling water cost	$0.0317/m^3 ($0.12/1000 gal)
Electrical energy cost	$0.05/KWH
Labor costs	$12.50/hour
Heating value	3.33 Kcal/g COD (6000 BTU/lb COD)
Oxygen transfer efficiency	90%

Previous experience with wet oxidation design (51) has indicated that batch results are applicable to continuous process design based on an oxygen transfer efficiency of 90% (11% excess air). Further, for a general waste such as sewage sludge or typical composite industrial waste streams, a heating value of 3.33 Kcal per gram of COD consumed is applicable. If detailed information on the composition of the waste stream and products were available, a more precise heating value could be determined.

PROCESS DESCRIPTION AND ANALYSIS

The wet oxidation process flow diagram shown in Figure 37 was synthesized to treat and recover energy from the composite waste stream. The process is generally similar to other wet oxidation processes (9,52) which have been employed for treatment of high COD wastes with energy recovered as process steam. The process diagram and equipment costs are based on a reactor consisting of a cascade of completely stirred tank reactors (CSTR's) (11) contained within a horizontal cylinder. However, the co-flow bubble tower reactor configuration could be employed in place of the cascade design.

In analyzing this process, certain variables were considered as set by external constraints. These variables were:

Feed stream: mass rate, temperature, pressure, COD concentration

Cooling and steam process water: temperature

Atmospheric air: temperature and pressure

Subsequently, material balances, energy balances and performance equations were written for each process component. These equations were written in terms of variables denoting the mass rates, concentrations, pressures and temperatures of the various streams as well as the pertinent equipment characteristics (reactor volume, heat exchanger area and exchange coefficients). This resulted in a total of 63 equations containing 70 variables, giving the process 7 degrees of freedom. The actual number of equations and variables is not significant; however, the excess of variables in relation to the number of equations i.e. the 7 degrees of freedom, is significant.

The following seven variables were then selected as design variables with the remaining 63 variables becoming system variables. The design variables selected were: oxygen transfer efficiency, reactor temperature, reactor liquid retention time, steam temperature, vapor condensate temperature, reactor uncondensable gas temperature and reactor feed temperature. Six of these variables were then fixed at reasonable values:

Oxygen transfer efficiency: 90%

Reactor temperature: 232°C

Reactor liquid detention time: 60 minutes based on liquid feed

Steam temperature: 138°C

Vapor condensate temperature: 32°C

Uncondensable gas temperature: 143°C

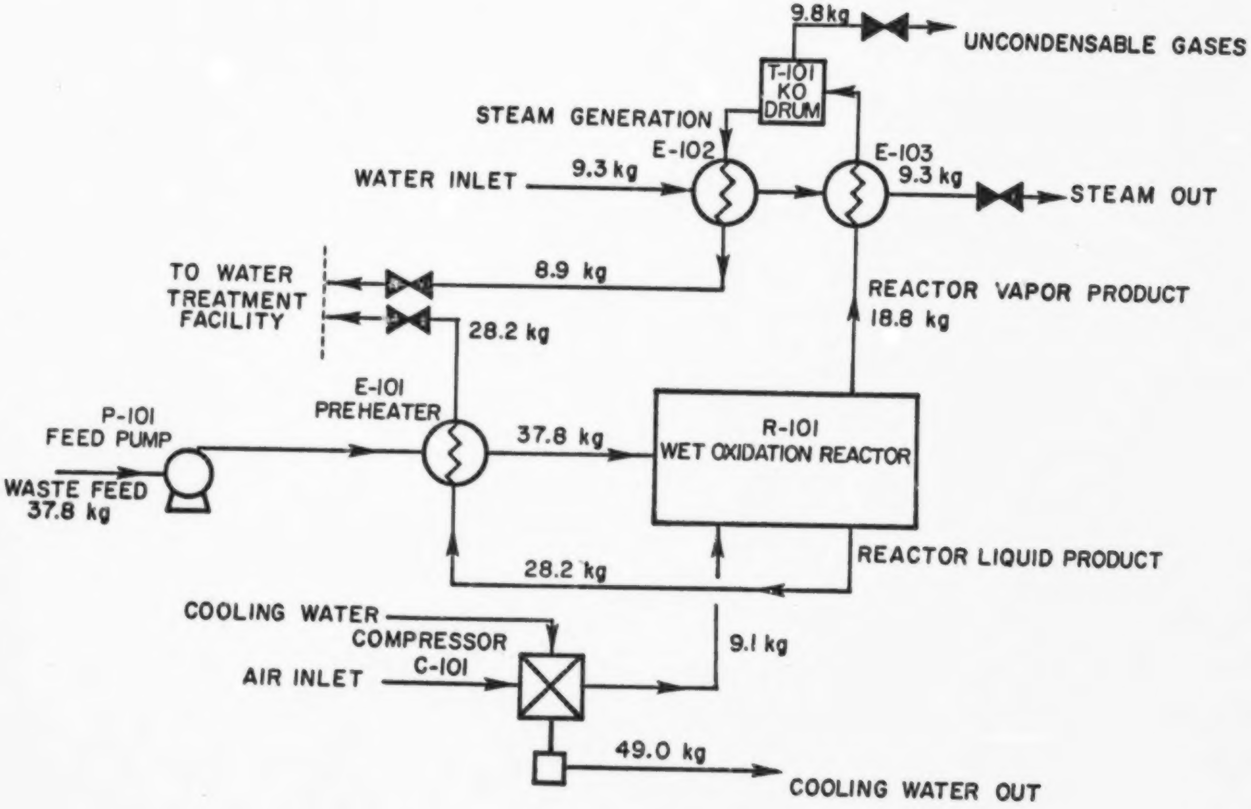

9.8 kg
UNCONDENSABLE GASES
T-101
KO
DRUM
STEAM GENERATION
E-102
E-103
WATER INLET
9.3 kg
9.3 kg
STEAM OUT
TO WATER
TREATMENT
FACILITY
8.9 kg
28.2 kg
REACTOR VAPOR PRODUCT
18.8 kg
P-101
FEED PUMP
E-101
PREHEATER
WASTE FEED
37.8 kg
37.8 kg
R-101
WET OXIDATION REACTOR
28.2 kg
REACTOR LIQUID PRODUCT
COOLING WATER
COMPRESSOR
C-101
AIR INLET
9.1 kg
49.0 kg
COOLING WATER OUT

Figure 37. Process Flow Diagram Showing Mass Rates (Basis 1 Minute).

The oxygen transfer efficiency of 90% is based on experience. The reactor temperature of 232°C and 1 hour residence time were based on the batch test results and resulted in a predicted 73% COD removal. The steam temperature of 138°C was based on process steam requirements and 32°C was selected as a reasonable vapor condensate temperature. The uncondensable gas temperature of 143°C was arbitrarily set between the reactor and condensate temperature.

This left the reactor feed temperature as the key design variable. With the other six design variables fixed, setting the reactor feed temperature will completely define the process. That is, given a reactor feed temperature, the material balance, energy balance and performance equations can be solved simultaneously with zero degrees of freedom.

Changes in the reactor feed temperature markedly affected the values calculated for the system variables. Figures 38 and 39 show the reactor pressure and mass rate of water vaporization as a function of reactor feed temperature. It is apparent that higher reactor feed temperatures lead to lower reactor pressures and higher rates of water vaporization within the reactor, both of which are favorable as far as reactor cost and energy recovery are concerned. However, attainment of a high reactor feed temperature requires increased area in the preheater heat exchanger. Figure 40 shows the estimated heat exchanger cost as a function of reactor feed temperature. Exchanger costs increased markedly with increasing feed temperature. In view of this, 173°C was selected as a reasonable reactor feed temperature. The temperatures, pressures, and mass rates shown in Figures 37 and 41 reflect the solution of the process balance and performance equations for a reactor feed temperature of 173°C. Further optimization might be possible by minor adjustments of the design variables.

EQUIPMENT SELECTION AND COST

Equipment vendors were contacted and requested to supply quotations for specific pieces of equipment meeting the requirements of the process design reflected in Figures 37 and 41. Key features and costs (December 1980) of the equipment selected are:

Compressor: Three stage reciprocatory machine with intercoolers; capacity of 7.1 m^3/min actual air; 80 KW (107 HP) power requirement; 49 Kg/min cooling water requirement; cost $77,800.

Feed Pump: Plunger type fitted with speed control; 9.7 KW (13 HP); cost $5600.

Preheater Heat Exchanger: Three titanium alloy shell and tube heat exchangers in parallel; total heat transfer area of 3.72 m^2; cost $22,900.

Reactor: Horizontal cylinder, 0.91 m diameter and 3.66 m long, divided by baffles into four chambers, each equipped with an agitator and air diffuser; constructed of titanium; headspace volume of 6%; cost $220,000.

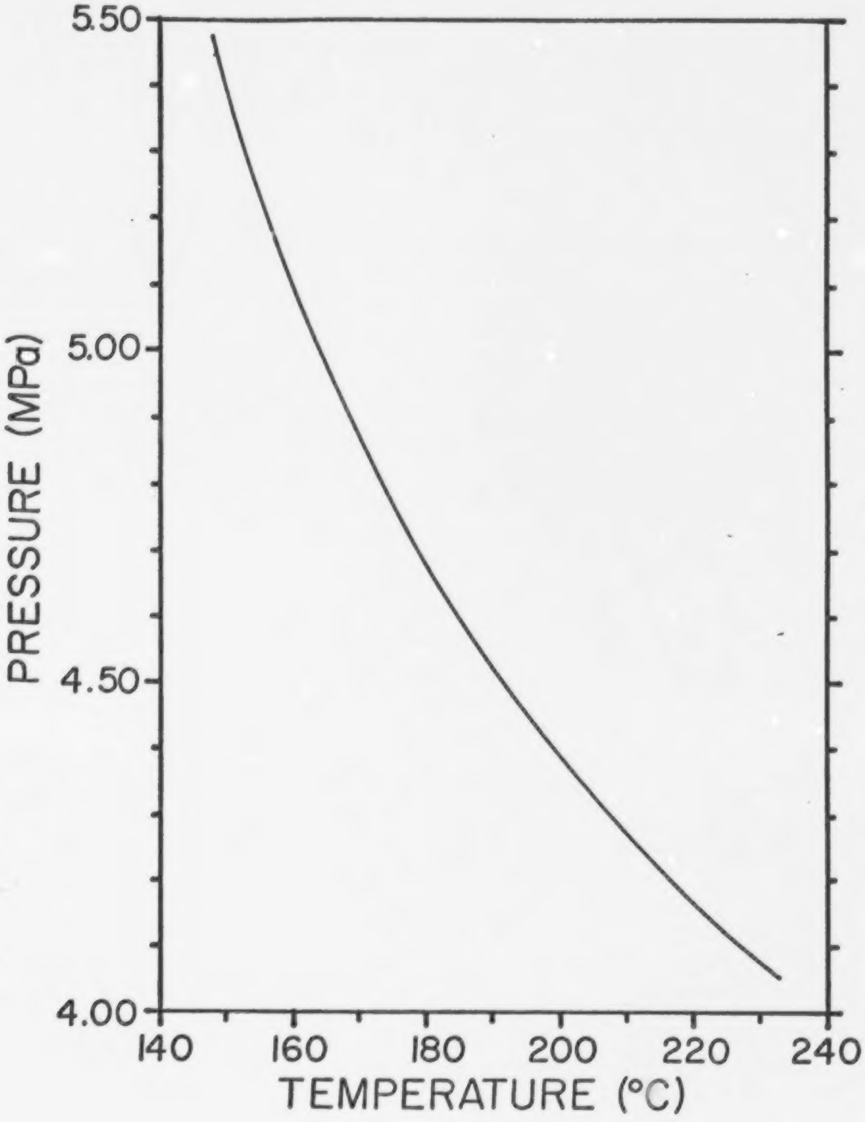


Figure 38. Variation of Reactor Pressure with Liquid Feed Inlet Temperature.

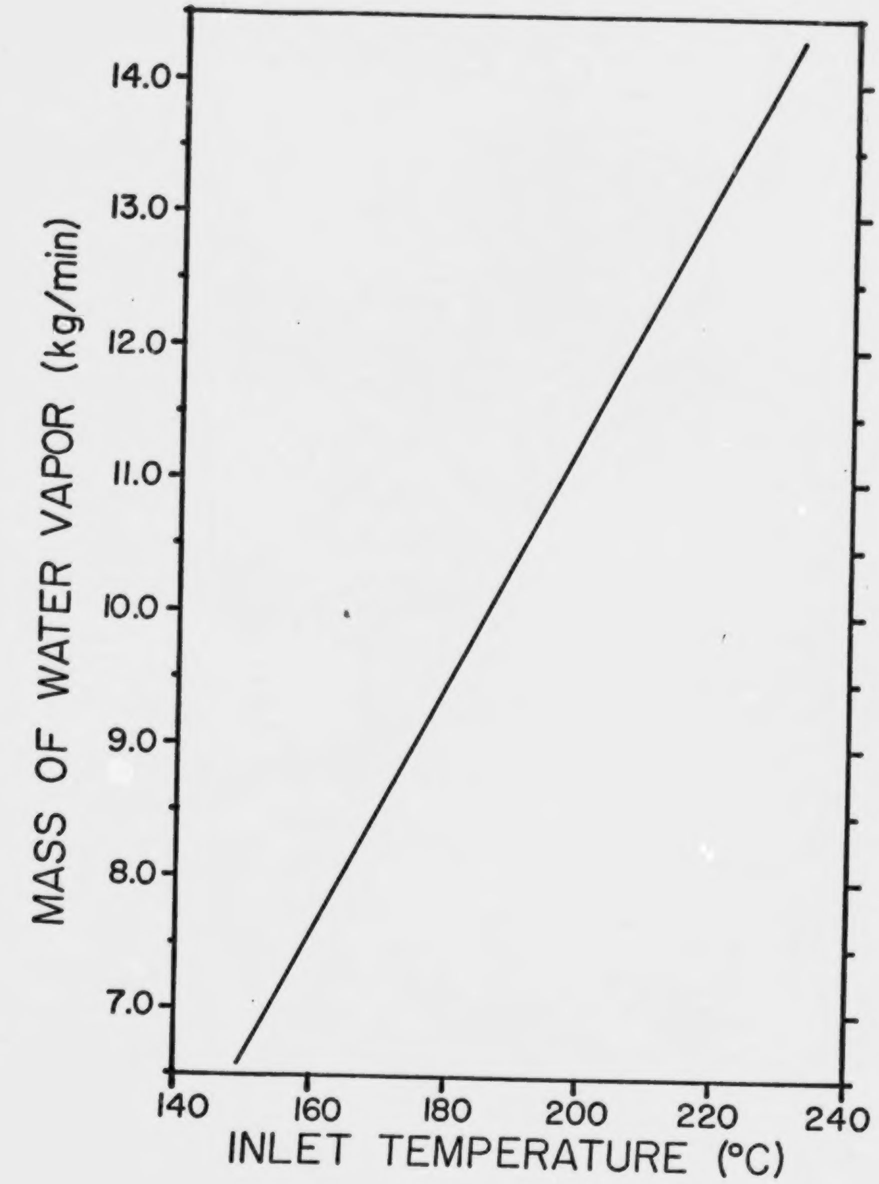


Figure 39. Variation of Mass Rate of Water in Reactor Vapor Product Stream with Reactor Feed Inlet Temperature.

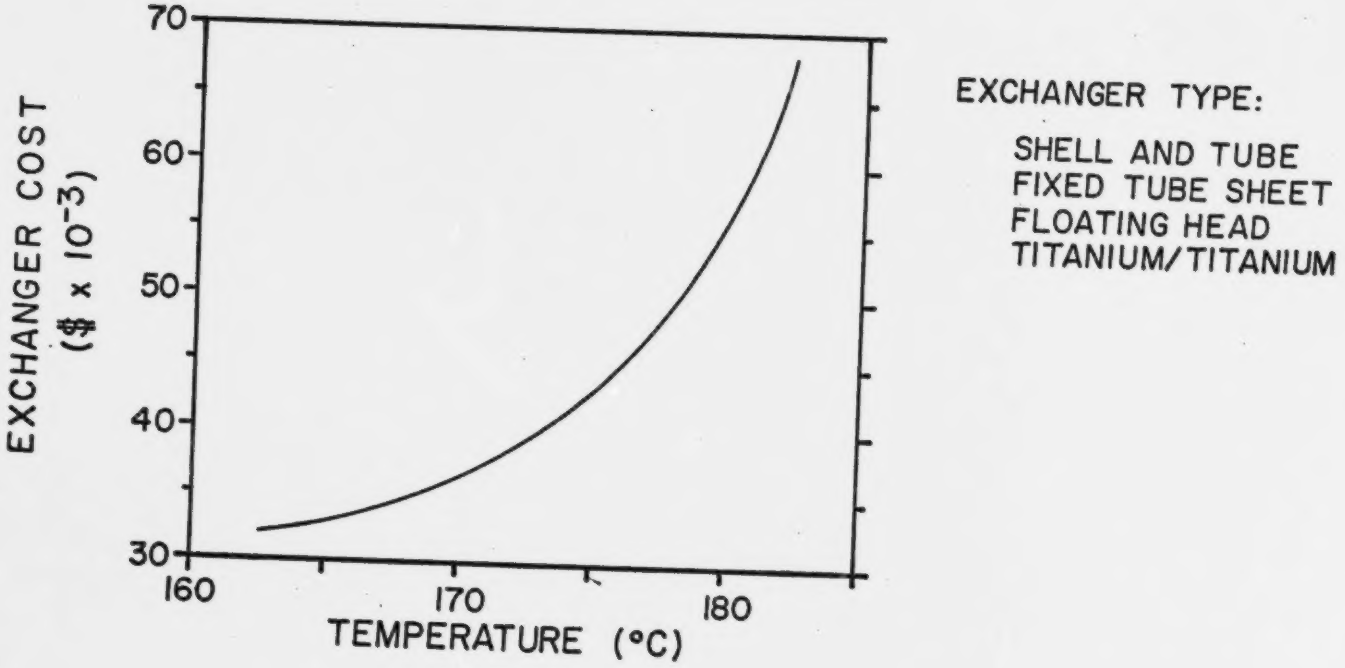


Figure 40. Feed Preheat Exchanger Cost in Thousands of Dollars versus Reactor Feed Temperature.

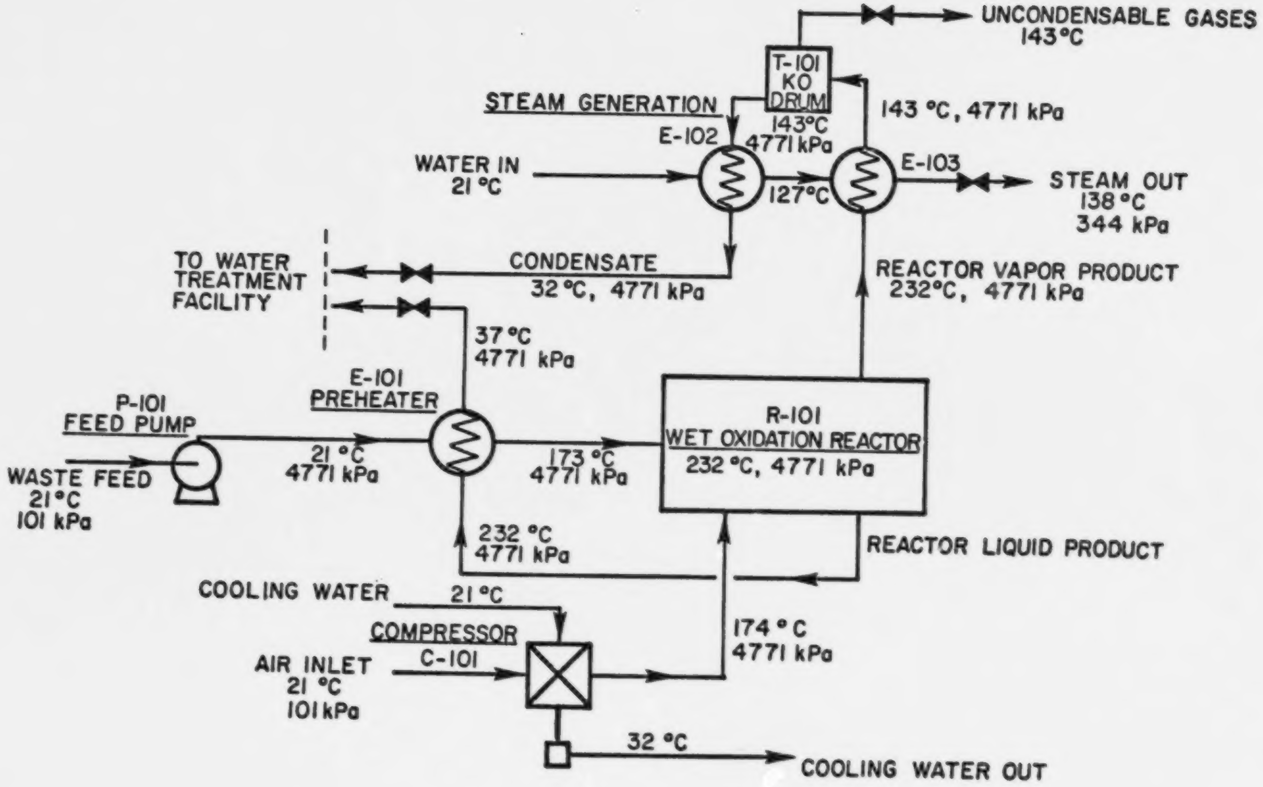

UNCONDENSABLE GASES
143°C
T-101
KO
DRUM
143°C
4771 kPa
143 °C, 4771 kPa
STEAM GENERATION
E-102
E-103
WATER IN
21 °C
127°C
STEAM OUT
138 °C
344 kPa
TO WATER
TREATMENT
FACILITY
CONDENSATE
32 °C, 4771 kPa
REACTOR VAPOR PRODUCT
232°C, 4771 kPa
37 °C
4771 kPa
E-101
PREHEATER
P-101
FEED PUMP
R-101
WET OXIDATION REACTOR
232 °C, 4771 kPa
WASTE FEED
21 °C
101 kPa
21 °C
4771 kPa
173 °C
4771 kPa
232 °C
4771 kPa
REACTOR LIQUID PRODUCT
COOLING WATER
21 °C
COMPRESSOR
C-101
AIR INLET
21 °C
101 kPa
174 °C
4771 kPa
32 °C
COOLING WATER OUT

Figure 41. Process Flow Diagram Showing Temperatures and Pressures.

Steam Generator: Composed of a feed water preheater, steam generator and knockout drum; preheater and generator are type 304 stainless steel shell and tube heat exchanger with heat transfer areas of 4.37 m^2 and 8.45 m^2, respectively; cost $8700.

ECONOMIC EVALUATION

A summary of purchased equipment cost (PEC) is given in Table 23. It is apparent that the reactor and compressor, taken together, account for almost 90% of the total PEC of $335,000.

TABLE 23. EQUIPMENT COST SUMMARY

Item	Purchased Equipment Cost (PEC)	Percent of PEC
Feed Pump	$5600	1.7
Compressor	$77,800	23.2
Preheater Heat Exchanger	$22,900	6.8
Reactor	$220,000	65.7
Steam Generator	$8700	2.6
Total PEC	$335,000	100.0

The total capital investment for this process is summarized in Table 24 and was estimated following the guidelines outlined by Peters and Timmerhaus (53). Costs were estimated based on cost factors typical of a fluid processing plant with special consideration given to the high operating pressures.

Direct costs were estimated from cost factors relating to the PEC. Installation costs, at 21% of the PEC, accounted for the foundations, supports and labor necessary for installation of the process. Instrumentation for the system is minimal and was estimated at 6% of the PEC. Although the amount of pipe required for the process is small, the piping cost estimate, at 30% of the PEC, was large because of the high pressures. The system is small and has been designed for an existing plant. Consequently the costs of electrical installation, yard improvements and service facilities were combined. Indirect costs were also estimated from cost factors based on PEC. Table 24 indicates that the wet oxidation process outlined in Figures 37 and 41 would require a total capital investment of $735,750.

TABLE 24. TOTAL CAPITAL INVESTMENT SUMMARY

Direct Costs	
Purchased Equipment (PEC)	$ 335,000
Installation (21% PEC)	70,350
Instrumentation (6% PEC)	20,100
Piping (30% PEC)	100,500
Electrical	
Yard Improvements (10% PEC)	33,500
Service Facilities	
Total Direct Cost	$ 559,450
Indirect Costs	
Engineering & Supervision (6% PEC)	$ 20,000
Construction Expense (15% PEC)	50,000
Contractor's Fee (8.4% PEC)	28,000
Contingency (13.4% PEC)	44,800
Total Indirect Cost	$ 142,800
Fixed Capital Investment	702,250
Working Capital (10% PEC)	33,500
Total Capital Investment	$ 735,750

Table 25 shows a summary of annual income and expenses for the process. Steam production is the only source of revenue, and based on 9.3 Kg/min of 344 KPa (50 psig) steam at a value of $13.21 per 1000 Kg ($6 per million BTU), yields an annual credit of $55,000. Operating expenses for this system consist of utilities, labor and maintenance. The compressor accounts for 89% of the annual $30,000 power cost. It was estimated that the process would require 0.5 posts occupied by 4.2 men. At $12.50 per hour plus 19% fringe benefits, this gives an annual labor cost of $65,000. Maintenance costs were not considered labor and were estimated at 7% of the total capital investment per year. Total operating expenses of $145,780 per year are partially offset by $55,000 per year income from power generation giving a net operating expense of $90,780 per year.

TABLE 25. ANNUAL INCOME AND OPERATING EXPENSE SUMMARY

Income	
Steam Generation	$55,000
Expenses	
Electricity ($0.05/KWH)	$30,000
Process Water	$780
Labor	$65,000
Maintenance	$50,000
Total Operating Expenses	$145,780
Net Operating Expenses	$90,780

Based on the cost data shown in Tables 24 and 25, the investor's interest rate of return (IIR) was determined as a function of treatment charges, i.e., the amount the wet oxidation system would have to charge in dollars per 1000 gallons treated waste to achieve a given return on investment.

The IIR calculations were based on:

Corporate tax rate: 48%

Investment tax credit taken in year zero: 10%

Double declining balance depreciation over 10 years

Project life: 15 years

Salvage value: zero

Figure 42 shows that, at a treatment charge of $30 per 1000 gallons, a zero rate of return is realized; whereas at a treatment charge of $69 per 1000 gallons ($0.16 per pound of COD removed), a 20% rate of return would be realized. It is reasonable to take 20% as a minimum acceptable return on investment. This means that, if the cost of the present or other alternative means for handling the waste is greater than $69 per 1000 gallons, or $0.16 per pound of COD removed, the industry can achieve a 20% return on investment by installing the wet oxidation system.

Figure 43 shows the results of a sensitivity analysis calculated using the $69 per 1000 gallons charge and 20% IIR as a base case. The IIR is least sensitive to changes in income and slightly more sensitive to changes in operating expenses. The system is most sensitive to changes in the capital investment.

Typical costs of secondary biological municipal wastewater treatment are on the order of $0.50 per 1000 gallons which is two orders of magnitude less than the $69 per 1000 gallons charge. However, typical municipal charges to industry are on the order of $0.05 to $0.10 per pound of COD removed which compares somewhat more favorably to the charge of $0.16 per pound of COD removal corresponding to the 20% IIR. In summary, the wet oxidation system does not appear to be an economically attractive alternative if it is feasible to discharge the wastewater to a biological wastewater treatment system.

On the other hand, if the waste is not acceptable at a biological treatment facility and the alternative is hauling as a hazardous waste under the Resource Recovery and Conservation Act regulations, the wet oxidation process appears to be attractive. Typical charges for hauling hazardous wastes are on the order of:

Barrelled Waste: $50 to $70 per 55 gallon drum plus $3 per loaded mile shipping

Bulk Waste: $0.55 to $0.75 per gallon plus $3 per loaded mile shipping

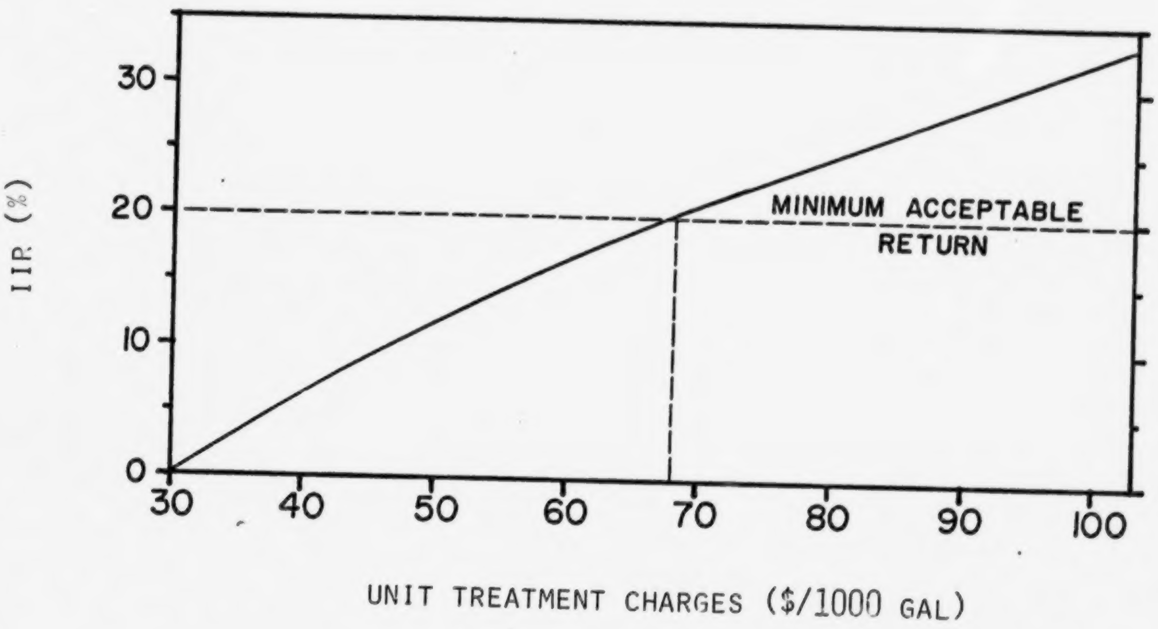


Figure 42. Variation of IIR with Treatment Charges. ($/1000 gal = 0.264 $/m^3)

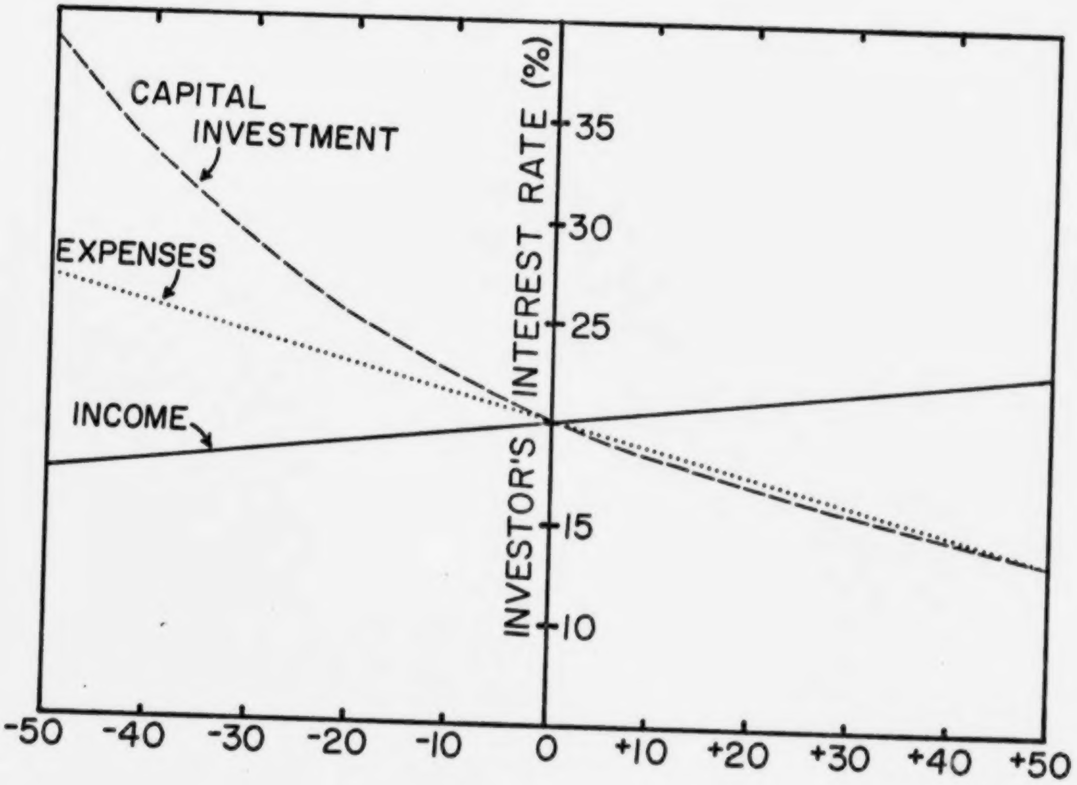


Figure 43. Sensitivity of Investor's Interest Rate with Respect to Changes in Capital Investment, Operating Expenses and Income.

Comparison of these charges with those shown for wet oxidation treatment in Table 26 indicates that the wet oxidation process is an economically attractive alternative to hauling as a hazardous waste.

TABLE 26. INFLUENCE OF WET OXIDATION TREATMENT CHARGES ON IIR

Treatment Charge, Dollars per				IIR
1000 gal	55 gal Drum	gal	lb COD Removed	(%)
30	1.65	0.03	0.07	0
50	2.75	0.05	0.12	12
70	3.85	0.07	0.17	21
90	4.95	0.09	0.21	29

Katzer et al. (57) presented an economic analysis of a catalytic (200°C, 4990 KP_a) wet oxidation system designed to remove phenol from a 555 gpm coke plant waste stream. Their estimated 1974 cost of $0.75 per 1000 gallons (approximately $1.15 per 1000 gallons adjusted to 1980) did not include labor, maintenance, overhead, taxes and power. This is significantly lower than the costs given in Table 26 because of these neglected costs and because of process differences, effects of scale and possible under estimation of reactor costs by Katzer et al.

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NOMENCLATURE

DIMENSIONS AND UNITS

atm = atmosphere

BTU = British thermal unit

^{o}C = degrees Celsius

cal = calorie

cm = centimeter

^{o}F = degrees Fahrenheit

g = gram

gal = gallon

hr = hour

HP = horse power

^{o}K = degrees Calvin

Kcal = kilocalorie

Kg = kilogram

KPa = kilopascal

KW = kilowatt

KWH = kilowatt hour

L = length

ℓ = liter

lb = pound

$\underline{M}$ = molarity

m = meter

$\underline{m}$ = mass

mg = milligram

min = minute

ml = milliliter

mm = millimeter

mol = gram mole

MPa = megapascal

nm = nanometer

psia = pounds per square inch, absolute

psig = pounds per square inch, gauge

rpm = revolutions per minute

sec = second

t = time

T = temperature

Δ = difference between two values

Σ = summation

ABBREVIATIONS

A = diffusing dissolved gas

B = dissolved substance

BOD = biochemical oxygen demand

BOD_5 = 5 day biochemical oxygen demand

COD = chemical oxygen demand

CSTR = completely stirred tank reactor

DCE = 1,2-dichloroethane

DMP = 1,2-dimethylphthalate

EC-50 = effective concentration of a compound being tested where 50% of the *Daphnia magna* are lying motionless on the bottom of the tank after 48 hours of exposure to the test compound

exp (x) = e^x

FID = flame ionization detector

GC = gas chromatograph

GC-MS = gas chromatograph-mass spectrophotometer

his^- = mutant strain of *Salmonella typhimurium* which can not synthesize histidine

his^+ = strain of *S. typhimurium* which can synthesize histidine

IIR = investor's interest rate of return

LC = liquid chromatograph

O.D. = outside diameter

PEC = purchased equipment cost

TOC = total organic carbon

2-CP = 2-chlorophenol

4-NP = 4-nitrophenol

95% C.L. = 95% confidence limits

SYMBOLS

a = interfacial area per unit volume, L^{-1}

A_f = frequency factor, $L^3 \, mol^{-1} \, t^{-1}$

A_H = constant used to calculate H_{O2}, dimensionless

B_H = constant used to calculate H_{O2}, dimensionless

C = aqueous concentration of specific substance, TOC or COD at time t, $\underline{m}\ L^{-3}$

C_B = concentration of dissolved substance in the bulk liquid, $\underline{m}\ L^{-3}$

C_g = concentration of specific substance in the gas phase, $\underline{m}\ L^{-3}$

C_H = constant used to calculate H_{O2}, dimensionless

C_{ifg} = inorganic carbon in final gas inventory, $\underline{m}$

C_{ifl} = inorganic carbon in final liquid inventory, $\underline{m}$

C_{igs} = inorganic carbon in gas samples and purges, $\underline{m}$

C_{ils} = inorganic carbon removed by liquid samples and purges, $\underline{m}$

C_o = aqueous concentration of specific substance, TOC or COD at time zero, $\underline{m}\ L^{-3}$

C_{of} = organic carbon in final liquid inventory, $\underline{m}$

C_{ogs} = organic carbon in gas samples and purges, $\underline{m}$

C_{ols} = organic carbon removed by liquid samples and purges, $\underline{m}$

C_t = total carbon injected, $\underline{m}$

C_{tr} = aqueous concentration of specific substance, TOC or COD at which the transition from the fast to slow reaction occurs, $\underline{m}\ L^{-3}$

C^* = aqueous residual concentration of specific substance, TOC or COD approached asymptotically as time approaches infinity, $\underline{m}\ L^{-3}$

C_A^* = equilibrium concentration of the diffusing gas in the liquid, $\underline{m}\ L^{-3}$

C_a^* = aqueous concentration of specific substance in equilibrium with the gas phase, $\underline{m}\ L^{-3}$

C_{a1}^* = aqueous concentration of specific substance in equilibrium with the gas phase at temperature 1, $\underline{m}\ L^{-3}$

C_{a2}^* = aqueous concentration of specific substance in equilibrium with the gas phase at temperature 2, $\underline{m}\ L^{-3}$

C_{O3}^* = equilibrium concentration of ozone in the liquid, $\underline{m}\ L^{-3}$

Cl^-_{rx} = chloride concentration in final liquid inventory, $\underline{m}\ L^{-3}$

Cl^-_{1-6} = chloride concentration in liquid samples and purges, $\underline{m}\ L^{-3}$

$CO_3^=$ = inorganic carbon in carbonate, $\underline{m}$

COD_f = COD in final liquid inventory, $\underline{m}$

COD_{ls} = COD removed by liquid samples and purges, $\underline{m}$

COD_o = theoretical COD of initial reactant injected, $\underline{m}$

COD_{rx} = COD concentration of final liquid inventory, $\underline{m}\ L^{-3}$

COD_u = oxygen used to accomplish reduction in COD, $\underline{m}$

COD_{1-6} = COD removed by liquid samples and purges, $\underline{m}\ L^{-3}$

D = constant used to calculate H_{O2}, dimensionless

D_A = diffusivity of the diffusing gas, $L^2\ t^{-1}$

D_B = diffusivity of the dissolved substance, $L^2\ t^{-1}$

D_{O2} = diffusivity of oxygen, $L^2\ t^{-1}$

D_{O3} = diffusivity of ozone, $L^2\ t^{-1}$

E = mass transfer enhancement factor, ratio of K_La in presence of reaction to K_La with no reaction, dimensionless

E_a = energy of activation, cal mol^{-1}

E_H = constant used in calculating H_{O2}, dimensionless

$$E_i = \left[1 + \frac{(D_B)\ (C_B)}{z\ (D_A)\ (C_A^*)}\right]\text{, dimensionless}$$

f_c = mass fraction of carbon in specific substance, dimensionless

f_{Cl} = mass fraction of chlorine in initial reactant, dimensionless

F_{CO} = fraction of carbon monoxide in dry gas purge or sample, dimensionless

F_{CO2} = fraction of carbon dioxide in dry gas purge or sample, dimensionless

f_o = mass fraction of oxygen required to completely oxidize one mole of initial reactant, dimensionless

F_{O2} = fraction of oxygen in dry gas purge or sample, dimensionless

F = ozone dosage rate, mol ozone (mol phenol initially present)$^{-1}$ (min)$^{-1}$

G = volumetric gas flow rate, L^3 t^{-1}

H = Henry's Law constant, defined by C_g/C_a^*, dimensionless

H_{CO2} = Henry's Law constant for carbon dioxide, atm L^3 mol^{-1}

H_{O2} = Henry's Law constant for oxygen, atm (mol fraction)$^{-1}$

H_1 = Henry's Law constant at temperature 1, dimensionless

H_2 = Henry's Law constant at temperature 2, dimensionless

$\bar{H}_{O2}$ = H_{O2} X 10^{-4}, atm (mol fraction)$^{-1}$

H^+ = hydrogen ion concentration, dimensionless

HCO_3^- = inorganic carbon in bicarbonate, $\underline{m}$

$H_2CO_3^*$ = inorganic carbon in carbonic acid plus aqueous carbon dioxide, $\underline{m}$

K_c = combined rate constant, mol phenol (mol ozone)$^{-1}$

K_L = overall mass transfer coefficient based on liquid film, L t^{-1}

k_o = reaction rate constant for wet oxidation, L^3 mol^{-1} t^{-1}

k_w = second order reaction rate constant for wet oxidation, L^3 mol^{-1} t^{-1}

K_1 = ionization constant for carbonic acid, dimensionless

K_2 = ionization constant for carbonic acid, dimensionless

k_o' = second order reaction rate constant for ozonation, gives r in terms of ozone, mol L^{-3} t^{-1}

K_La = overall volumetric mass transfer coefficient based on the liquid film, t^{-1}

$(K_La)_{O2}$ = overall volumetric mass transfer coefficient for oxygen, t^{-1}

$(K_La)_{O3}$ = overall volumetric mass transfer coefficient for ozone, t^{-1}

L_{fl} = chlorine in final liquid inventory, $\underline{m}$

L_{ls} = chlorine removed in liquid samples and purges, $\underline{m}$

L_{lss} = chlorine removed by liquid samples and purges containing initial reactant, $\underline{m}$

L_t = total chlorine injected, $\underline{m}$

M = $(D_A)(k_o')(C_B)/K_L^2$, dimensionless

m_f = removal parameter for phasic fast reaction kinetic model, t^{-1}

m_r = removal parameter for ozonation, t^{-1}

M_s = mass of substance injected, $\underline{m}$

m_s = removal parameter for phasic slow reaction kinetic model, t^{-1}

m_1 = removal parameter for first order kinetic model, t^{-1}

m_2 = removal parameter for modified first order kinetic model, t^{-1}

MW_c = molecular weight of carbon, $\underline{m}$ mol^{-1}

MW_o = molecular weight of oxygen, $\underline{m}$ mol^{-1}

MW_s = molecular weight of specific substance, $\underline{m}$ mol^{-1}

MW_w = molecular weight of water, $\underline{m}$ mol^{-1}

O_{fg} = oxygen in final gas inventory, $\underline{m}$

O_{fl} = oxygen in final liquid inventory, $\underline{m}$

O_{gs} = oxygen removed by gas samples and purges, $\underline{m}$

O_h = oxygen injected with reactant charge calculated by injection system, $\underline{m}$

O_{hrh} = oxygen injected with reactant charge calculated by reactor headspace, $\underline{m}$

O_{h1} = oxygen in injection system before injection, $\underline{m}$

O_{h2} = oxygen in injection system after injection, $\underline{m}$

O_{id} = oxygen in cold initial reactor content, $\underline{m}$

O_{ih} = oxygen in headspace of cold reactor, $\underline{m}$

O_{ls} = oxygen removed with liquid samples and purges, $\underline{m}$

O_t = total oxygen present after injection, $\underline{m}$

O_2 = aqueous concentration of oxygen, $\underline{m}$ L^{-3}

O_3 = aqueous concentration of ozone, $\underline{m}$ L^{-3}

P_{COD} = oxygen pressure required to oxidize reactant, atm

P_{O2} = partial pressure of oxygen in initial cold reactor, atm

P_{rai} = reactor pressure after injection, atm

P_{rbi} = reactor pressure before injection, atm

P_s = steam pressure at cold reactor temperature, atm

P_{sai} = steam pressure at reactor temperature after injection, atm

P_{sbi} = steam pressure at reactor temperature before injection, atm

P_t = total pressure of cold reactor after last cold gas sample is taken, atm

P_{ts} = total reactor pressure after sample collection, atm

P_{u1-6} = volume of liquid purge, L^3

P_{v1} = vapor pressure of a pure substance at temperature 1, atm

P_{v2} = vapor pressure of a pure substance at temperature 2, atm

P_1 = oxygen pressure of pressurized injection system before injection, atm

P_2 = oxygen pressure of pressurized injection system after injection, atm

R = ideal gas constant, L^3 atm mol^{-1} T^{-1}

r = rate of reaction per unit volume for wet oxidation, mol L^{-3} t^{-1}

R_o = mass utilization rate of ozone, $\underline{m}$ t^{-1}

R_{rx} = initial reactant concentration in final liquid inventory, $\underline{m}$ L^{-3}

R_s = mass utilization rate of specific substance, $\underline{m}$ t^{-1}

R_{1-6} = initial reactant concentration in liquid samples and purges, $\underline{m}$ L^{-3}

s = standard error, t^{-1}

S_{1-6} = volume of liquid sample, L^3

T_a = ambient temperature, T

T_{abs} = absolute temperature, T

T_{ai} = temperature of injection system after injection, T

T_{bi} = temperature of injection system prior to injection, T

T_{CR} = temperature of cold reactor, t

t_r = time of reaction or stripping, t

T_{rai} = temperature of reactor after injection, T

T_{rbi} = temperature of reactor before injection, T

t_{tr} = time at which the transition from the fast to slow reaction occurs, t

T_1 = temperature at condition 1, T

T_2 = temperature at condition 2, T

TOC_f = TOC of cooled reactor content, $\underline{m}\ L^{-3}$

TOC_{1-6} = TOC of liquid samples and purges, $\underline{m}\ L^{-3}$

V_{fl} = volume of cooled reactor content, L^3

V_G = volume of gas in the reactor headspace, L^3

V_{gs} = volume of gas sample cylinder, L^3

V_{hs} = volume of reactor headspace at injection, L^3

V_{h1} = volume of injection system before injection, L^3

V_{h2} = volume of injection system after injection, L^3

V_{il} = volume of cold initial reactor liquid content, L^3

V_L = volume of liquid in the reactor, L^3

V_t = total reactor volume, L^3

W = maximal ozone transfer rate, $\underline{m}\ t^{-1}$

z = number of moles of substance B, mol

$1/\bar{T}_{bi} = (1/T_{bi}) \text{ X } 10^3$, T^{-1}

ρ_w = density of water, $\underline{m}\ L^{-3}$

APPENDIX A

MATERIAL BALANCE PROCEDURE AND NUMERICAL EXAMPLE

CARBON BALANCE

$$\%\ \text{Carbon Recovery} = \left[\frac{C_{ols} + C_{of} + C_{igs} + C_{ifg} + C_{ifl}}{C_t}\right] 100$$

1. Total carbon injected: C_t, $\underline{m}$

$$C_t = (M_s)(f_c)$$

where: M_s = mass of substance injected, $\underline{m}$

f_c = mass fraction of carbon, dimensionless

2. Organic carbon removed by liquid samples and purges: C_{ols}, $\underline{m}$

Sample	Time (t)	Purge Volume (L^3)	Sample Volume (L^3)	TOC ($\underline{m}\ L^{-3}$)
1	0	P_{u1}	S_1	TOC_1
2	2	P_{u2}	S_2	TOC_2
3	5	P_{u3}	S_3	TOC_3
4	15	P_{u4}	S_4	TOC_4
5	30	P_{u5}	S_5	TOC_5
6	60	P_{u6}	S_6	TOC_6

$$C_{ols} = TOC_1 (P_{u1} + S_1 + P_{u2}) + TOC_2 (S_2 + P_{u3}) + TOC_3 (S_3 + P_{u4}) + \ldots + TOC_6 (S_6)$$

3. Organic carbon in final liquid inventory: C_{of}, $\underline{m}$

$$C_{of} = (TOC_f)(V_{fl})$$

where: TOC_f = TOC of cooled reactor content, $\underline{m}\ L^{-3}$

V_{fl} = volume of cooled reactor content, L^3

4. Inorganic carbon removed by gas sampling: $\sum_{i=1}^{4} C_{igs}$, $\underline{m}$

Inorganic carbon in each gas purge and sample: C_{igs}, $\underline{m}$

$$C_{igs} = \frac{(MW_c)(F_{CO2} + F_{CO})(P_{ts})(V_{gs})}{R(T_a)}$$

where: MW_c = molecular weight of carbon, $\underline{m}\ mol^{-1}$

F_{CO2} = fraction of CO_2 in dry gas purge or sample, dimensionless

F_{CO} = fraction of CO in dry gas purge or sample, dimensionless

P_{ts} = total reactor pressure after sample collection, atm

V_{gs} = volume of gas sample cylinder, L^3

R = ideal gas constant, L^3 atm mol^{-1} T^{-1}

T_a = ambient temperature, T

5. Inorganic carbon in final gas inventory: C_{ifg}, $\underline{m}$

$$C_{ifg} = \frac{(MW_c)(P_t - P_s)(V_t - V_{fl})(F_{CO2} + F_{CO})}{(R)(T_{CR})}$$

where: P_t = total pressure of cold reactor after the last cold gas sample is taken, atm

P_s = steam pressure at cold reactor temperature, atm

V_t = total reactor volume, L^3

T_{CR} = temperature of cold reactor, T

6. Inorganic carbon in final liquid inventory: C_{ifl}, m

C_{ifl} = Carbon in $H_2CO_3^*$ + carbon in HCO_3^- + carbon in $CO_3^=$

A. Inorganic carbon in carbonic acid plus aqueous CO_2: $H_2CO_3^*$, m

$$H_2CO_3^* = \frac{MW_c(V_{fl})(F_{CO2})(P_t - P_s)}{(H_{CO2})}$$

where: H_{CO2} = Henry's Law constant for CO_2, atm L^3 mol^{-1}

This is calculated using the following equation (54):

$\log (1/H_{CO2}) = 2385.73/T_{CR} - 14.0184 + 0.01526 \times T_{CR}$

B. Inorganic carbon in HCO_3^-: HCO_3^-, m

$$HCO_3^- = \frac{K_1(H_2CO_3^*)}{H^+}$$

where: K_1 = ionization constant for carbonic acid, dimensionless

This is calculated using the following equation (54):

$-\log (K_1) = 3404.71/T_{CR} - 14.8435 + 0.03276 \times T_{CR}$

H^+ = hydrogen ion concentration, dimensionless

This is calculated by the following equation:

$H^+ = 10^{-pH}$

C. Inorganic carbon in $CO_3^=$: $CO_3^=$, $\underline{m}$

$$CO_3^= = \frac{K_2(HCO_3^-)}{H^+}$$

where: K_2 = ionization constant for carbonic acid, dimensionless
This is calculated from the following equation developed from data given by Snoeyink and Jenkins (55):
$-\log (K_2) = 3399.04/T_{CR} - 9.75629 + 0.0291134 \times T_{CR}$

OXYGEN BALANCE

$$\% \text{ Oxygen Recovery} = \left[\frac{O_{gs} + O_{fg} + O_{fl} + COD_u}{O_t}\right] 100$$

1. Total oxygen present after injection: O_t, $\underline{m}$

$$O_t = O_{id} + O_{ih} + O_h$$

A. Oxygen in cold initial reactor content: O_{id}, $\underline{m}$

$$O_{id} = \frac{(V_{il})(P_{O2})(MW_o)(\rho_w)}{(MW_w)(H_{O2})}$$

where: V_{il} = volume of cold initial reactor liquid content, L^3

P_{O2} = partial pressure of oxygen in initial cold reactor, atm

MW_o = molecular weight of oxygen, $\underline{m}\ mol^{-1}$

ρ_w = density of water, $\underline{m}\ L^{-3}$

MW_w = molecular weight of water, $\underline{m}\ mol^{-1}$

H_{O2} = Henry's Law constant for O_2, atm (mol fraction)$^{-1}$
This is calculated using the following equation (44):
$A_H(\log \bar{H}_{O2})^2 + B_H(1/\bar{T}_{bi})^2 + C_H(\log \bar{H}_{O2})(1/\bar{T}_{bi}) +$
$D(\log \bar{H}_{O2}) + E_H(1/\bar{T}_{bi}) -1 = 0$

where: $\bar{H}_{02} = H_{02} \times 10^{-4}$, atm (mol fraction)$^{-1}$

$1/\bar{T}_{bi} = (1/T_{bi}) \times 10^{3}$, T

T_{bi} = temperature of injection system prior to injection, T

A_H = -0.0005943, dimensionless

B_H = -0.1470, dimensionless

C_H = -0.05120, dimensionless

D = -0.1076, dimensionless

E_H = 0.8447, dimensionless

B. Oxygen in headspace of cold reactor: 0_{ih}, m

$$0_{ih} = \frac{MW_o(P_{02})(V_t - V_{i1})}{(R) \quad (T_{bi})}$$

C. Oxygen injected with reactant charge: 0_h, m

$$0_h = 0_{h1} - 0_{h2}$$

Oxygen in injection system before injection: 0_{h1}, m

$$0_{h1} = \frac{(MW_o)(P_1)(V_{h1})}{(R)\ (T_{bi})}$$

where: P_1 = oxygen pressure of pressurized injection system before injection, atm

V_{h1} = volume of injection system before injection, L^3

Oxygen in injection system after injection: 0_{h2}, m

$$O_{h2} = \frac{(MW_o)(P_2)(V_{h2})}{(R)\ (T_{ai})}$$

where: P_2 = oxygen pressure of pressurized injection system after injection, atm

V_{h2} = volume of injection system after injection, L^3

T_{ai} = temperature of the injection system after injection, T

Due to occasional leaks in the injection system, better results can sometimes be obtained by applying the ideal gas law to the reactor headspace. Therefore:

$$O_{hrh} = \frac{(MW_o)(V_{hs})}{(R)} \left[\frac{(P_{rbi} - P_{sbi})}{T_{rbi}} - \frac{(P_{rai} - P_{sai})}{T_{rai}} \right]$$

where: O_{hrh} = oxygen injected with reactant charge calculated from reactor headspace, $\underline{m}$

V_{hs} = volume of reactor headspace at injection, L^3

Calculated by taking in account the steam pressure and specific volume of liquid water at the reactor temperature.

P_{rbi} = reactor pressure before injection, atm

P_{sbi} = steam pressure at reactor temperature before injection, atm

P_{rai} = reactor pressure after injection, atm

P_{sai} = steam pressure at reactor temperature after injection, atm

T_{rbi} = temperature of reactor before injection, T

T_{rai} = temperature of reactor after injection, T

2. Oxygen removed by gas samples and purges: $\sum_{i=1}^{4} O_{gs}$, $\underline{m}$

Oxygen in each gas purge and sample: O_{gs}, $\underline{m}$

$$O_{gs} = \frac{(MW_o)(F_{02})(P_{ts})(V_{gs})}{(R)\ (T_a)}$$

where: F_{02} = fraction of oxygen in dry gas purge or sample, dimensionless

3. Oxygen in final gas inventory: O_{fg}, $\underline{m}$

$$O_{fg} = \frac{(MW_o)(F_{02})(P_t - P_s)(V_t - V_{fl})}{(R)\ (T_a)}$$

4. Oxygen in final liquid inventory: O_{fl}, $\underline{m}$

$$O_{fl} = \frac{(MW_o)(V_{fl})(\rho_w)(F_{02})(P_t - P_s)}{(MW_w)\ (H_{02})}$$

5. Oxygen used to accomplish reduction in COD: COD_u, $\underline{m}$

$$COD_u = COD_o - COD_{ls} - COD_f$$

A. Theoretical COD of initial reactant injected: COD_o, $\underline{m}$

$$COD_o = \frac{(M_s)(f_o)(MW_o)}{(MW_s)}$$

where: f_o = mass fraction of oxygen required to completely oxidize 1 mole of initial reactant, dimensionless

MW_s = molecular weight of initial reactant, $\underline{m}$ mol^{-1}

B. COD removed by liquid samples and purges: COD_{ls}, $\underline{m}$

Sample	Time (t)	Purge Volume (L^3)	Sample Volume (L^3)	COD ($\underline{m}\ L^{-3}$)
1	0	P_{u1}	S_1	COD_1
2	2	P_{u2}	S_2	COD_2
3	5	P_{u3}	S_3	COD_3
4	15	P_{u4}	S_4	COD_4
5	30	P_{u5}	S_5	COD_5
6	60	P_{u6}	S_6	COD_6

$$COD_{1s} = COD_1 (P_{u1} + S_1 + P_{u2}) + COD_2 (S_2 + P_{u3}) + COD_3 (S_3 + P_{u4}) + \ldots + COD_6 (S_6)$$

C. COD in final liquid inventory: COD_f, $\underline{m}$

$$COD_f = (COD_{rx})(V_{f1})$$

where: COD_{rx} = COD concentration in final liquid inventory, $\underline{m}\ L^{-3}$

CHLORINE BALANCE

$$\%\ \text{chlorine recovery} = \left[\frac{L_{1s} + L_{f1} + L_{1ss}}{L_t}\right] 100$$

1. Total chlorine injected: L_t, $\underline{m}$

$$L_t = M_s (f_{c1})$$

where: f_{c1} = mass fraction of chlorine in initial reactant, dimensionless

2. Chlorine removed by liquid samples and purges: L_{1s}, $\underline{m}$

Sample	Time (t)	Purge Volume (L^3)	Sample Volume (L^3)	Chloride ($\underline{m}\ L^{-3}$)
1	0	P_{u1}	S_1	Cl^-_1
2	2	P_{u2}	S_2	Cl^-_2
3	5	P_{u3}	S_3	Cl^-_3
4	15	P_{u4}	S_4	Cl^-_4
5	30	P_{u5}	S_5	Cl^-_5
6	60	P_{u6}	S_6	Cl^-_6

$$L_{1s} = Cl^-_1\ (P_{u1} + S_1 + P_{u2}) + Cl^-_2\ (S_2 + P_{u3}) + Cl^-_3\ (S_3 + P_{u4}) + \ldots + Cl^-_6\ (S_6)$$

3. Chlorine in final liquid inventory: L_{f1}, $\underline{m}$

$$L_{f1} = (Cl^-_{rx})(V_{f1}) + (R_{rx})(f_{Cl})(V_{f1})$$

where: Cl^-_{rx} = chloride concentration in final liquid inventory, $\underline{m}\ L^{-3}$

R_{rx} = initial reactant concentration in final liquid inventory, $\underline{m}\ L^{-3}$

4. Chlorine removed by liquid samples and purges containing initial reactant: L_{1ss}, $\underline{m}$

Sample	Time (t)	Purge Volume (L^3)	Sample Volume (L^3)	Reactant ($\underline{m}\ L^{-3}$)
1	0	P_{u1}	S_1	R_1
2	2	P_{u2}	S_2	R_2
3	5	P_{u3}	S_3	R_3
4	15	P_{u4}	S_4	R_4
5	30	P_{u5}	S_5	R_5
6	60	P_{u6}	S_6	R_6

$$L_{1ss} = \Big[R_1\,(P_{u1} + S_1 + P_{u2}) + R_2\,(S_2 + P_{u3}) + R_3\,(S_3 + P_{u4}) + \cdots + R_6\,(S_6)\Big]\, f_{Cl}$$

MATERIAL BALANCE EXAMPLE

Reactant: 2-chlorophenol

Temperature: 204°C

Experiment: 13

Carbon Balance

1. Total carbon injected: C_t ....2.80 g

   (5.0 g 2CP)(0.558) = 2.80 g

2. Organic carbon removed by liquid samples and purges: C_{ols} ....0.371 g

Sample	Time (min)	Purge Volume (ℓ)	Sample Volume (ℓ)	TOC (mg/ℓ)
1	0	0.010	0.023	1174
2	2	0.012	0.022	2592
3	5	0.010	0.022	2308
4	15	0.006	0.030	1863
5	30	0.010	0.030	1498
6	60	0.013	0.025	1256

$$C_{ols} = \Big[1174\ \text{mg}/\ell\ (0.010 + 0.023 + 0.012)\ \ell + 2592\ (0.022 + 0.01) + 2308\ (0.022 + 0.006) + 1863\ (0.03 + 0.01) + 1498\ (0.030 + 0.013) + 1256\ (0.025)\Big]\ 10^{-3}\ (\text{g/mg}) = 0.371\ \text{g}$$

3. Organic carbon in final liquid inventory: C_{of}...........1.179 g

$$C_{of} = (1498\ \text{mg}/\ell)(0.787\ \ell)(10^{-3}\ \text{g/mg}) = 1.179\ \text{g}$$

4. Inorganic carbon removed by gas sampling: $\sum_{i=1}^{4} C_{igs}$.....0.317 g

A. Hot purge

$$C_{igs} = \frac{(12\ \text{g/mol})(38.07\ \text{atm})(0.04\ \ell)(0.147 + 0.010)}{(0.082\ \ell\ \text{atm/mol}\ {}^{o}\text{K})(293\ {}^{o}\text{K})} = 0.119\ \text{g}$$

B. Hot sample

$$C_{igs} = \frac{(12)(35.63)(.04)(0.174 + 0.013)}{0.082\ (293)} = 0.133\ \text{g}$$

C. Cold purge

$$C_{igs} = \frac{(12)(10.52)(.04)(0.155 + 0.012)}{0.082\ (293)} = 0.035 \text{ g}$$

D. Cold sample

$$C_{igs} = \frac{(12)(10.12)(.04)(0.135 + 0.011)}{0.082\ (293)} = 0.030 \text{ g}$$

$$\sum_{i=1}^{4} C_{igs} = 0.119 + 0.133 + 0.035 + 0.030 = 0.317 \text{ g}$$

5. Inorganic carbon in headspace of cold reactor: C_{ifg}.........0.729 g

$$C_{ifg} = \frac{(12 \text{ g/mol})(9.7 \text{ atm} - 0.04 \text{ atm})(1.85\ \ell - 0.787\ \ell)(0.135 + 0.011)}{(0.082\ \ell \text{ atm/mol } ^{o}\text{K})(301\ ^{o}\text{K})}$$

$$= 0.729 \text{ g}$$

6. Inorganic carbon in final liquid inventory: C_{ifl}......0.425 g

A. Inorganic carbon in $H_2CO_3^*$

$$H_2CO_3^* = \frac{(12 \text{ g/mol})(0.787\ \ell)(0.147)(9.7 \text{ atm} - 0.04 \text{ atm})}{(31.56 \text{ atm } \ell/\text{mol})} = 0.425 \text{ g}$$

B. Inorganic carbon in HCO_3^-

$$HCO_3^- = \frac{(5 \times 10^{-7})(0.425 \text{ g})}{0.01} = 2.12 \times 10^{-5} \text{ g}$$

C. Inorganic carbon in $CO_3^=$

$$CO_3^= = \frac{(5.02 \times 10^{-11})(2.12 \times 10^{-5} \text{ g})}{0.01} = 1.07 \times 10^{-13} \text{ g}$$

$$C_{ifl} = 0.425 + 2.12 \times 10^{-5} + 1.07 \times 10^{-13} = 0.425 \text{ g}$$

$$\% \text{ carbon recovery} = \left[\frac{0.371 + 1.179 + 0.317 + 0.729 + 0.425}{2.8}\right] 100$$

$$= 108\%$$

Oxygen Balance

1. Total oxygen present after injection: O_t....................17.707 g

   A. Oxygen in cold initial reactor content

$$O_{id} = \frac{(0.9\ \ell)(0.2\text{ atm})(32\text{ g/mol})(1000\text{ g}/\ell)}{(18\text{ g/mol})(35000\text{ atm/mol fraction})} = 0.009 \text{ g}$$

   B. Oxygen in headspace of cold reactor

$$O_{ih} = \frac{(32\text{ g/mol})(0.2\text{ atm})(1.85\ \ell - 0.90\ \ell)}{(0.082\ \ell\text{ atm/mol }^{o}\text{K})(287\ ^{o}\text{K})} = 0.258 \text{ g}$$

   C. Oxygen injected with reactant charge

   Oxygen in injection system before injection

$$O_{h1} = \frac{(32\text{ g/mol})(42.50\text{ atm})(2.1\ \ell)}{(0.082\ \ell\text{ atm/mol }^{o}\text{K})(287\ ^{o}\text{K})} = 121.36 \text{ g}$$

   Oxygen in injection system after injection

$$O_{h2} = \frac{(32)(34.74)(2.2)}{(0.082)(287)} = 103.92 \text{ g}$$

$$O_h = 121.36 - 103.92 = 17.44 \text{ g}$$

$$O_t = 0.009 + 0.258 + 17.44 = 17.707 \text{ g}$$

2. Oxygen removed by gas samples and purges: $\sum_{i=1}^{4} O_{gs}$....3.711 g

A. Hot purge

$$0_{gs} = \frac{(32\ \text{g/mol})(0.719)(38.07\ \text{atm})(0.04\ \ell)}{(0.082\ \ell\ \text{atm/mol}\ ^{o}\text{K})(293\ ^{o}\text{K})} = 1.458\ \text{g}$$

B. Hot sample

$$0_{gs} = \frac{(32)(.732)(35.63)(.04)}{(0.082)(293)} = 1.389\ \text{g}$$

C. Cold purge

$$0_{gs} = \frac{(32)(.764)(10.52)(.04)}{(0.082)(293)} = 0.428\ \text{g}$$

D. Cold sample

$$0_{gs} = \frac{(32)(.799)(10.25)(.04)}{(0.082)(293)} = 0.436\ \text{g}$$

$$\sum_{i=1}^{4} 0_{gs} = 1.458 + 1.389 + 0.428 + 0.436 = 3.711\ \text{g}$$

3. Oxygen in final gas inventory: 0_{fg}.....10.637 g

$$0_{fg} = \frac{(32\ \text{g/mol})(0.799)(9.7\ \text{atm} - 0.04\ \text{atm})(1.85\ \ell - 0.787\ \ell)}{(0.082\ \ell\ \text{atm/mol}\ ^{o}\text{K})(301\ ^{o}\text{K})}$$

$$= 10.637\ \text{g}$$

4. Oxygen in final liquid inventory: 0_{fl}.....0.304 g

$$0_{fl} = \frac{(32\ \text{g/mol})(0.787\ \ell)(1000\ \text{gm}/\ell)(0.799)(9.7\ \text{atm} - 0.04\ \text{atm})}{(18\ \text{g/mol})\ (35500\ \text{atm/mol fraction})}$$

$$= 0.304\ \text{g}$$

5. Oxygen used to accomplish reduction in COD:

COD_u........4.387 g

A. Theoretical COD of initial reactant injected

$$COD_o = \frac{(5\ g\ 2CP)(7)(32\ g/mol)}{(128.6\ g/mol)} = 8.709\ g$$

B. COD removed by liquid samples and purges

Sample	Time (min)	Purge Volume (ℓ)	Sample Volume (ℓ)	COD (mg/ℓ)
1	0	0.010	0.023	3665
2	2	0.012	0.022	7888
3	5	0.010	0.022	7569
4	15	0.006	0.030	5418
5	30	0.010	0.030	4382
6	60	0.013	0.025	3585

$$COD_{ls} = \Big[3665\ mg/\ell\ (0.010 + 0.023 + 0.012)\ \ell + 7888\ (0.022 + 0.01) + 7569\ (0.022 + 0.006) + 5418\ (0.03 + 0.01) + 4382\ (0.03 + 0.013) + 3585\ (0.025)\Big]\ (10^{-3}\ g/mg) = 1.124\ g$$

C. COD in final liquid inventory

$$COD_f = \frac{(4063\ mg/\ell)(0.787\ \ell)}{(1000\ mg/g)} = 3.198\ g$$

$$COD_u = 8.709 - 1.124 - 3.198 = 4.387\ g$$

$$\%\ Oxygen\ Recovery = \left[\frac{3.711 + 10.637 + 0.304 + 4.387}{17.707}\right] 100$$

$$= 108\%$$

Chlorine Balance

1. Total chlorine injected: L_t.........1.375 g

L_t = (5 g 2CP)(0.275) = 1.375 g

2. Chlorine removed by liquid samples and purges: L_{1s}..........0.104 g

Sample	Time (min)	Purge Volume (ℓ)	Sample Volume (ℓ)	Chloride (mg/ℓ)
1	0	0.010	0.023	10
2	2	0.012	0.022	15
3	5	0.010	0.022	260
4	15	0.006	0.030	652
5	30	0.010	0.030	979
6	60	0.013	0.025	1105

$$L_{1s} = \Big[10 \text{ mg}/\ell\ (0.01 + 0.023 + 0.012)\ \ell + 15\ (0.022 + 0.01) + 260\ (0.022 + 0.006) + 652\ (0.03 + 0.01) + 979\ (0.03 + 0.013) + 1105\ (0.025)\Big]\ (10^{-3} \text{ g/mg}) = 0.104 \text{ g}$$

3. Chlorine in final liquid inventory: L_{fl}.........1.067 g

$$L_{fl} = \frac{(1026 \text{ mg}/\ell)(0.787\ \ell) + (1199 \text{ mg}/\ell)(0.275)(0.787\ \ell)}{(1000 \text{ mg/g})} = 1.067 \text{ g}$$

4. Chlorine removed by liquid samples and purges containing initial reactant: L_{1ss}..........0.161 g

Sample	Time (min)	Purge Volume (ℓ)	Sample Volume (ℓ)	2CP (mg/ℓ)
1	0	0.010	0.023	2586
2	2	0.012	0.022	5194
3	5	0.010	0.022	4014
4	15	0.006	0.030	2529
5	30	0.010	0.030	1506
6	60	0.013	0.025	1026

$$\begin{aligned} L_{1ss} &= \big[2586\ \text{mg}/\ell\ (0.010 + 0.023 + 0.012)\ \ell + 5194\ (0.022 + 0.01) + \\ &\quad 4014\ (0.022 + 0.006) + 2529\ (0.03 + 0.01) + \\ &\quad 1506\ (0.03 + 0.013) + 1026\ (0.025)\big]\ (0.275)(10^{-3}\ \text{g/mg}) \\ &= 0.161\ \text{g} \end{aligned}$$

$$\begin{aligned} \%\ \text{Chlorine Recovery} &= \left[\frac{0.104 + 1.067 + 0.161}{1.375}\right] 100 \\ &= 97\% \end{aligned}$$

APPENDIX B

MATERIAL BALANCE RESULTS AND BREAKDOWN FROM WET OXIDATION EXPERIMENTS

TABLE B-1. PHENOL MATERIAL BALANCE RESULTS

Experiment	Conditions	Percent Recovery	
		Carbon	Oxygen
2	204°C	86	120
3	204°C	88	105
4	232°C	84	226
5	232°C	128	119[a]
7	260°C	117	172
8	232°C High pH	-	124[a]
10	204°C Copper Catalyst	131	145[a]
11	260°C Copper Catalyst	95	131
	Mean	104	143
	95% C.L.*	89 - 119	115 - 170

[a] Calculated using headspace parameters of reactor at operating temperature; all others using injection system parameters.

* Mean 95% confidence limit.

TABLE B-2. 1,2-DIMETHYLPHTHALATE MATERIAL BALANCE RESULTS

Experiment	Conditions	Percent Recovery	
		Carbon	Oxygen
32	204°C	78	106[a]
33	232°C	85	107
34	260°C	112	71
35	232°C High pH	64	117[a]
36	204°C, 50 mg/ℓ Copper Catalyst	83	80
37	204°C, 500 mg/ℓ Copper Catalyst	100	109
38	260°C, 100 mg/ℓ Copper Catalyst	64	121
39	260°C, 500 mg/ℓ Copper Catalyst	92	121
	Mean	85	104
	95% C.L.*	73 - 96	91 - 117

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[a] Calculated using headspace parameters of reactor at operating temperature; all others using injection system parameters.

* Mean 95% confidence limit.

TABLE B-3. 4-NITROPHENOL MATERIAL BALANCE RESULTS

Experiment	Conditions	Percent Recovery Carbon	Percent Recovery Oxygen
26	232°C	114	105

TABLE B-4. 1,2-DICHLOROETHANE MATERIAL BALANCE RESULTS

Experiment	Conditions	Percent Recovery Carbon	Percent Recovery Oxygen	Percent Recovery Chlorine
40	204°C	82	114	80
41	232°C	89	79	94
42	260°C	102	69	89
44	232°C Copper Catalyst	104	88	96
	Mean	94	88	90
	95% C.L.*	84 - 105	69 - 107	83 - 97

* Mean 95% confidence limit.

TABLE B-5. PHENOL MATERIAL BALANCE BREAKDOWN

Experiment	C_t^*	C_{ols}^*	C_{of}^*	C_{igs}^*	$C_{ifg} + C_{ifl}^*$	% Rec'd	O_t^*	O_{gs}^*	$O_{fl} + O_{fg}^*$	COD_u^*	% Rec'd
2	4.438	0.568	0.599	0.488	2.142	85.6	21.036	3.200	10.714	11.350	120.1
3	4.438	0.438	0.601	0.639	2.206	87.5	21.361	2.639	7.950	11.865	105.1
4	3.443	0.543	0.340	0.543	1.475	84.2	8.436	3.669	7.182	8.189	225.7
5	3.826	0.373	0.422	0.924	3.164	127.7	15.217[a]	2.577	5.608	9.860	118.6
7	3.443	0.402	0.470	0.923	2.217	116.5	13.819	5.141	10.129	8.544	172.3
8	3.826	0.569	1.105	0.079	26.877	748.4	11.133[a]	2.482	3.741	7.564	123.8
10	3.443	0.403	0.261	0.714	3.135	131.1	12.690[a]	2.433	6.426	9.593	145.4
11	3.443	0.161	0.201	0.668	2.229	94.6	23.587	6.403	14.533	9.917	130.8

* In grams.

[a] Calculated using headspace parameters of reactor at operating temperature; all others using injection system parameters.

TABLE B-6. 1,2-DIMETHYLPHTHALATE MATERIAL BALANCE BREAKDOWN

Experiment	C_t*	C_{ols}*	C_{of}*	C_{igs}*	$C_{ifg} + C_{ifl}$*	% Rec'd	O_t*	O_{gs}*	$O_{fl} + O_{fg}$*	COD_u*	% Rec'd
32	3.090	0.476	1.911	0.002	0.007	77.5	11.960[a]	3.384	9.466	-0.128	106.4
33	0.618	0.163	0.356	0.000	0.008	85.2	7.984	3.567	5.122	-0.165	106.8
34	0.742	0.252	0.581	0.000	0.000	112.3	9.788	4.490	2.389	0.041	70.7
35	0.742	0.170	0.287	0.001	0.019	64.4	8.680[a]	3.109	7.164	-0.108	117.1
36	3.090	0.403	0.411	0.404	1.337	82.7	17.602	2.238	5.762	6.120	80.2
37	3.090	0.449	0.283	0.174	2.173	99.6	21.255	2.200	14.623	6.408	109.3
38	0.742	0.076	0.000	0.146	0.252	63.9	15.090	6.399	9.974	1.832	120.6
39	2.941	0.139	0.224	0.974	1.356	91.5	12.932	3.413	4.620	7.649	121.3

* In grams.

a Calculated using headspace parameters of reactor at operating temperature; all others using injection system parameters.

TABLE B-7. 4-NITROPHENOL MATERIAL BALANCE BREAKDOWN

Experiment	C_t*	C_{ols}*	C_{of}*	C_{igs}*	C_{ifg} + C_{ifl}*	% Rec'd	O_t*	O_{gs}*	O_{fl} + O_{fg}*	COD_u*	% Rec'd
26	2.588	0.429	0.610	0.413	1.505	114.3	20.278	4.433	10.330	6.441	104.6

* In grams.

TABLE B-8. 1,2-DICHLOROETHANE MATERIAL BALANCE BREAKDOWN

Experiment	C_t*	C_{ols}*	C_{of}*	C_{igs}*	C_{ifg} + C_{ifl}*	% Rec'd	O_t*	O_{gs}*	O_{fl} + O_{fg}*	COD_u*	% Rec'd
40	1.218	0.199	0.738	0.014	0.055	82.5	18.085	4.565	15.130	1.010	114.5
41	1.213	0.180	0.710	0.069	0.117	88.6	16.205	2.937	8.408	1.495	79.2
42	1.213	0.234	0.452	0.256	0.302	102.5	20.682	5.388	7.176	1.632	68.6
44	1.213	0.205	0.682	0.104	0.272	104.2	20.455	4.838	11.813	1.426	88.4

* In grams.